Supporting Information for:

Reversible C–N Bond Formation in the Zirconium-Catalyzed Intermolecular Hydroamination of 2-Vinylpyridine

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General Considerations

All air and moisture sensitive compounds were manipulated under inert N\textsubscript{2} atmosphere using an MBraun LABmaster glovebox or standard Schlenk techniques. Glassware was allowed to dry in a 160 °C oven prior to transferring to the glovebox or Schlenk manifold. Toluene and hexanes were passed through an activated alumina column under N\textsubscript{2} gas, collected in a Teflon sealed Straus flask, and sparged with N\textsubscript{2} for 30 minutes prior to use. Benzene-\textit{d}\textsubscript{6} and toluene-\textit{d}\textsubscript{8} were dried over sodium metal and distilled under N\textsubscript{2} and collected in a Teflon sealed Straus flask prior to use. J. Young NMR tubes (8” x 5 mm) with Teflon screw-caps were used for NMR reactions. \textit{\textsuperscript{1}}H and \textit{\textsuperscript{13}}C\{\textit{\textsuperscript{1}}H\} NMR spectra were collected using a Bruker 300 MHz or 400 MHz Avance spectrometer at 298 K unless otherwise noted. Chemical shifts, \(\delta\), are reported relative to the corresponding residual protio solvent in parts per million (ppm). Coupling constants, \(J\), are given in Hertz (Hz). Signal multiplicity is reported using the following abbreviations: \(s =\) singlet, \(d =\) doublet, \(t =\) triplet, \(q =\) quartet, \(sep =\) septet, \(m =\) multiplet, and \(br =\) broad. For van’t Hoff experiments, \(T_1\) relaxation times for the relevant signals were estimated using a spin-echo pulse sequence and relaxation delays were extended accordingly during \textit{\textsuperscript{1}}H NMR data collection. Mass spectra (MS) were collected using a Kratos MS-50 spectrometer equipped with an electron impact (EI, 70 eV) source, and fragments are given in mass per charge number (\textit{m/z}). Elemental analysis (EA) was performed with a Thermo Flash 2000 Elemental Analyzer. The elemental composition values are given in percentages (%). Single crystal X-ray diffraction data were collected using a Bruker X8 APEX or Bruker APEX DUO diffractometer. All chemicals were purchased from commercial sources and used without further purification, and those which were not already dried and stored under inert atmosphere were dried and degassed via the freeze-pump-thaw method before use. All amines and 2-vinylpyridine were dried over calcium hydride and distilled under N\textsubscript{2} before degassing via the freeze-pump-thaw method and bringing them into the glovebox or using them on the Schlenk manifold. Tetrabenzylzirconium(IV)\textsuperscript{1} and compounds \textsuperscript{1,2,3} and \textsuperscript{3,4} were prepared according to literature methods. Crystals of \textsuperscript{2} suitable for X-ray diffraction studies were grown from a concentrated toluene solution at −35 °C.
Synthesis of Complexes

Synthesis of 4: A 20 mL vial was charged with bis(amido) complex 3 (0.165 g, 0.309 mmol) before dissolving in ~5 mL toluene via gentle heating and vigorous swirling to give a clear, colourless solution. 2-Vinylpyridine (0.033 g, 0.31 mmol) was then added directly to the concentrated solution of 3 using ~0.5 mL toluene for quantitative transfer, causing an immediate colour change to bright orange. The vial was then placed in a freezer at −35 °C for several days, during which time bright orange crystals suitable for X-ray diffraction precipitated out of solution. After removing the supernatant, the crystals were washed with cold hexanes (5 x ~0.25 mL) and the residual solvent was allowed to evaporate, giving 0.120 g of material (61% yield). 

$^1$H NMR (C$_6$D$_6$, 400 MHz) δ = 7.04 (br d, 6.5 Hz, 1H), 6.23 (br d, J = 9.0 Hz, 1H), 6.21 (ddd, J = 9.0, 5.4, 1.6 Hz, 1H), 5.20 (ddd, J = 6.5, 5.4, 1.6 Hz, 1H), 4.19 (t, J = 7.1 Hz, 1H), 3.62 (br sep, J = 6.7 Hz, 4H), 3.44 (d, J = 11.5 Hz, 2H), 3.25 (d, J = 11.5 Hz, 2H), 3.22 (br m, 2H), 3.11 (br s, 6H), 2.61 (br s, 6H), 1.25 (d, J = 6.7 Hz, 12H), 1.17 (d, J = 6.7 Hz, 12H), 0.90 (br s, 3H); $^{13}$C NMR (C$_6$D$_6$, 100 MHz) δ = 167.3, 156.3, 146.9, 127.4, 121.1, 96.3, 79.9, 59.2, 57.8, 57.3, 46.6, 45.4, 36.8, 28.2, 22.2, 22.1, 21.5. The molecular ion was not observed by MS, instead the ion corresponding to a loss of 2-vinylpyridine was observed: MS(EI) m/z 532 [M − C$_7$H$_7$N]+, m/z 488 [M − C$_7$H$_7$N − N(CH$_3$)$_2$]+; Anal Calcd for C$_{36}$H$_{57}$N$_7$O$_2$Zr: N, 15.34; C, 56.38; H, 8.99. Found: N, 14.99; C, 56.50; H, 8.92.
**Synthesis of 5 in situ:** To a ~250 µL toluene-\textit{d}_8 solution of dibenzyl complex 2 (0.011 g, 0.017 mmol), pyrrolidine (0.004 g, 0.05 mmol) was added using ~250 µL toluene-\textit{d}_8 for quantitative transfer, causing a change to bright yellow before turning to pale yellow and then colourless over a period of 10 minutes. The reaction was found to be complete after 1 hour by \textit{^1}H NMR spectroscopy. \textit{^1}H NMR (C\textsubscript{7}D\textsubscript{8}, 400 MHz) \( \delta = 3.58\) (sep, 6.7 Hz, 4H), 3.48 (br m, 12H), 3.19 (br s, 4H), 2.06 (br s, 1H), 1.62 (br m, 12H), 1.28 (d, \( J = 6.7 \) Hz, 24H), 0.96 (br s, 6H); \textit{^13}C NMR (C\textsubscript{7}D\textsubscript{8}, 100 MHz) \( \delta = 168.8\), 57.6, 51.2, 46.7, 36.7, 26.9, 25.5, 22.4.

![](image)

**Synthesis of 6:** A 20 mL vial was charged with dibenzyl complex 2 (0.099 g, 0.16 mmol) before dissolving in ~7 mL hexanes via gentle heating and vigorous swirling to give a clear, pale yellow solution. Pyrrolidine (0.024 g, 0.33 mmol) was then added dropwise to the concentrated solution of 2 while stirring using ~2 mL hexanes for quantitative transfer, immediately turning it bright yellow and then gradually to pale yellow over a period of an hour. After stirring for a total of 4 hours, the volatiles were removed \textit{in vacuo} to give a colourless powder with a small amount of highly soluble pale-yellow solid (pyrrolidine adduct 5). Recrystallization in hexanes at –35 °C for several days and isolation of the colourless crystals resulted in 0.076 g of 6 (82% yield). Similar recrystallization in toluene was carried out to achieve crystals suitable for X-ray diffraction. \textit{^1}H NMR (C\textsubscript{6}D\textsubscript{6}, 300 MHz) \( \delta = 3.96\) (m, 8H), 3.52 (sep, 6.7 Hz, 4H), 3.03 (br s, 4H), 1.70 (m, 8H), 1.28 (d, \( J = 6.7 \) Hz, 24H), 0.88 (br s, 6H); \textit{^13}C NMR (C\textsubscript{6}D\textsubscript{6}, 75 MHz) \( \delta = 171.0\), 57.8, 52.7, 46.8, 36.8, 27.2, 24.8, 22.2; MS(EI) \( m/z \) 584 [M\textsuperscript{+}], \( m/z \) 514 [M – N(CH\textsubscript{2})\textsubscript{4}]\textsuperscript{+}. Satisfactory elemental analysis could not be obtained: Anal Calcd for C\textsubscript{54}H\textsubscript{108}N\textsubscript{12}O\textsubscript{4}Zr\textsubscript{2}: N, 14.34; C, 55.34; H, 9.29. Found: N, 14.47; C, 55.94; H, 9.72.
Synthesis of 7: A 20 mL vial was charged with dibenzyl complex 2 (0.202 g, 0.322 mmol) and suspended in ~3 mL toluene. Pyrrolidine (0.046 g, 0.64 mmol) was then added dropwise to the colourless solution using ~3 mL toluene for quantitative transfer, turning it bright yellow and then gradually to pale yellow over 15 minutes. The vial was shaken to assist dissolving. The volatiles were then removed in vacuo to give 6 as a colourless powder. 2-Vinylpyridine (0.071 g, 0.68 mmol) was then dissolved in ~3.5 mL toluene and added to the solid, turning the solution bright orange. Immediate formation of poly(vinylpyridine) was also observed. The vial was then placed in the freezer at −35 °C for several days, during which time orange crystals suitable for X-ray diffraction precipitated out of solution in addition to crude, insoluble material. X-ray crystallography revealed 7, but efforts to isolate it on a suitable scale to characterize it by NMR spectroscopy were futile as decomposition to 6 and polymer involving unidentified intermediates occurred spontaneously in solution. Extraction of the orange compound from the insoluble material with toluene, filtration through diatomaceous earth, and rapid removal of the volatiles in vacuo resulted in an orange-yellow material that was subjected to mass spectrometry: MS(EI) m/z 584 [M – C7H7N]+, m/z 514 [M – C7H7N – N(CH2)4]+. Elemental analysis could not be obtained.

Synthesis of 8: A 20 mL vial was charged with dibenzyl complex 2 (0.104 g, 0.165 mmol) before dissolving in ~7 mL hexanes via gentle heating and vigorous swirling to give a clear, pale yellow solution. Piperidine (0.028 g, 0.33 mmol) was then added dropwise to the concentrated solution of 2 while stirring using ~1 mL hexanes for quantitative transfer, immediately turning it bright yellow and then gradually to colourless over
a period of 5 minutes. After stirring for a total of 3 hours, the vial was placed in a freezer at –35 °C for several days and isolation of the colourless crystals suitable for X-ray diffraction resulted in 0.061 g of 8 (61% yield). $^1$H NMR (C$_6$D$_6$, 300 MHz) $\delta$ = 3.82 (br m, 8H), 3.50 (sep, 6.7 Hz, 4H), 3.04 (s, 4H), 1.72 (br m, 12H), 1.25 (d, $J$ = 6.7 Hz, 24H), 0.91 (br s, 6H); $^{13}$C NMR (C$_6$D$_6$, 75 MHz) $\delta$ = 171.0, 57.9, 52.4, 46.8, 36.6, 30.2, 26.8, 25.0, 22.3; MS(EI) m/z 612 [M$^+$], m/z 528 [M – N(CH$_2$)$_5$]$^+$; Anal Calcd for C$_{29}$H$_{38}$N$_6$O$_2$Zr: N, 13.69; C, 56.73; H, 9.52. Found: N, 13.83; C, 56.69; H, 9.63.
NMR Tube Experiments

Catalytic Hydroamination of 2-Vinylpyridine with Pyrroolidine: To separate small vials, toluene-$d_8$ (0.4715 g), dibenzyl complex 2 (0.025 mmol), 2-vinylpyridine (0.5 mmol), and pyrroolidine (0.55 mmol) were all weighed. Using the toluene-$d_8$ for quantitative transfer, the amine was transferred to the complex before adding 2-vinylpyridine to the mixture. The solution was then stirred at room temperature for 6 hours before transferring to a J. Young tube to determine the conversion by $^1$H NMR spectroscopy.

Stoichiometric Hydroamination of 2-Vinylpyridine with Dimethylamine: Complex 1 (0.016 g, 0.027 mmol) was transferred to a J. Young tube with ~1.25 mL toluene-$d_8$ before transferring 2-vinylpyridine (0.003 g, 0.03 mmol) to the same tube with ~150 $\mu$L toluene-$d_8$, turning the solution bright orange. The J. Young tube was then inverted continuously at room temperature and checked by $^1$H NMR spectroscopy periodically.

Stoichiometric Hydroamination of 2-Vinylpyridine with Pyrroolidine: After taking the $^1$H NMR spectrum of the in situ generated 5 after 1 hour (vide supra), 2-vinylpyridine (0.002 g, 0.02 mmol) was
added, turning the colourless solution orange. After 2 hours, the reaction was determined to be complete by 
$^1H$ NMR spectroscopy.

Reaction of 2-Vinylpyridine with 8: Bis(amido) complex 8 (0.008 g, 0.01 mmol) was transferred to a J. Young tube with ~250 $\mu$L toluene-$d_8$ before transferring 2-vinylpyridine (0.001 g, 0.01 mmol) to the same tube with ~450 $\mu$L toluene-$d_8$; no colour change was observed. The J. Young tube was then checked by $^1H$ NMR spectroscopy periodically. The only new signals observed were those resulting from the polymerization of 2-vinylpyridine.

Generation of 7 in situ: To a small vial, 2 (0.011 g, 0.018 mmol) was added and then dissolved in ~250 $\mu$L toluene-$d_8$. Pyrrolidine (0.003 g, 0.04 mmol) was then added, turning it bright yellow immediately and then pale yellow over 10 minutes. After transferring the solution to a J. Young tube, 2-vinylpyridine (0.002 g, 0.02 mmol) was added, turning it bright orange. VT $^1H$ NMR was then performed on the solution.

Catalytic Hydroamination of 2-Vinylpyridine with Piperidine: To separate small vials, toluene-$d_8$ (0.4712 g), dibenzyl complex 2 (0.025 mmol), 2-vinylpyridine (0.5 mmol), and piperidine (0.55 mmol) were all weighed. Using the toluene-$d_8$ for quantitative transfer, the amine was transferred to the complex
before adding 2-vinylpyridine to the mixture. The solution was then stirred at room temperature for 6 hours before transferring to a J. Young tube to determine the conversion by $^1$H NMR spectroscopy.

**Previous Literature and Preliminary Results**

**Scheme S1. A) Known Hydroamination Catalysts and (B) Initial Catalytic Studies with Alkenes**

**A) Schafer 2009, 2011: Catalysts for Hydroamination of Aminoalkenes/Alkynes**

**B) Catalytic Hydroamination of 2-Vinylpyridine with Pyrroldine using Catalyst 2**

1.1 [Chemical Structure] + [Chemical Structure] $\xrightarrow{5 \text{ mol\% 2}}$ 5 mol\% 2 0.5 mL toluene-$d_8$ r.t., 6 h >99% conversion
Van’t Hoff Data

Complex 4: To determine the $K_{eq}$ values at each temperature, the relative integrations of the Hc proton of 4 and the Hb proton of 2-vinylpyridine (see Figure S19 below) were measured and used to calculate the equilibrium constants (Table S1). Only the largest three temperatures are used as the integration of Hb is zero at the other three temperatures.

Table S1. Relevant parameters for construction of the van’t Hoff plot for complex 4.

| $T$ (°C) | Hc Integration | Hb Integration | $K_{eq}$ | $T$ (K) | $1/T$ (1/K) | ln($K_{eq}$) |
|---------|----------------|----------------|---------|---------|-------------|--------------|
| 25.5    | 1.00           | 0.76           | 1.7     | 298.7   | 0.003348    | 0.55         |
| 13.8    | 1.00           | 0.32           | 9.8     | 286.9   | 0.003485    | 2.28         |
| 2.2     | 1.00           | 0.11           | 83      | 275.4   | 0.003631    | 4.41         |

Sample calculation for $K_{eq}$ ($T = 25.54$ °C):

$$K_{eq} = \frac{1.00}{(0.76 \times 0.76)} = 1.7$$

Next, ln($K_{eq}$) was plotted versus $1/T$ to obtain the van’t Hoff plot (Figure S1). The equation of the line and associated errors were determined using the LINEST equation in Excel.

![Figure S1. Plot of ln($K_{eq}$) versus $1/T$ (van’t Hoff plot) for complex 4.](image)

Using the van’t Hoff equation, ln($K_{eq}$) = $-\Delta H^\circ / R T + \Delta S^\circ / R$ where $R = 8.3145 \times 10^{-3}$ kJ/mol•K, the enthalpy of reaction $\Delta H^\circ$ can be determined from the slope of the line in Figure S1 and the standard error in the slope (600 K, obtained from the LINEST equation):
\[ \Delta H^o = -1 \times \text{slope} \times R = -113. \pm 5. \text{ kJ/mol} \]

Similarly, the entropy of reaction \( \Delta S^o \) can be determined from the intercept of the line in Figure S1 and the standard error in the intercept (2, obtained from the LINEST equation):

\[ \Delta S^o = \text{intercept} \times R = -0.38 \pm 0.02 \text{ kJ/mol}\cdot\text{K} \]

Using the Gibbs free energy equation, \( \Delta G^o = \Delta H^o - T \Delta S^o \), the free energy can be calculated for \( T = 298 \text{ K} \) to compare to the computed free energy for a reversible C–N bond forming step in Mg-catalyzed hydroamination.\(^5\) The calculated errors in \( \Delta H^o \) and \( \Delta S^o \) can be used and converting to kcal/mol gives the free energy:

\[ \Delta G^o = -0.36 \pm 0.03 \text{ kJ/mol at 298 K}; \text{computed } \Delta G^o = 9.2 \text{ kcal/mol at 298 K} \]

These values are quite different, with this Zr system showing slightly exergonic C–N bond formation compared to an endergonic process in the Mg system.

**Complex 7:** To determine the \( K_{eq} \) values at each temperature, the relative integrations of the H\(_c\) proton of 7 (analogous to that of 4) and the H\(_b\) proton of 2-vinylpyridine (see Figure S18 below) were measured and used to calculate the equilibrium constants (Table S2). The lowest temperature is excluded as the integration of H\(_b\) is zero.

**Table S2.** Relevant parameters for construction of the van’t Hoff plot for complex 7.

| \( T \) (°C) | \( H_c \) Integration | \( H_b \) Integration | \( K_{eq} \) | \( T \) (K) | \( 1/T \) (1/K) | \( \ln(K_{eq}) \) |
|-------------|----------------------|----------------------|-----------|-------------|----------------|----------------|
| 25.54       | 1.00                 | 10.90                | 0.00842   | 298.7       | 0.003348       | -4.778         |
| 13.77       | 1.00                 | 2.41                 | 0.172     | 286.9       | 0.003485       | -1.759         |
| 2.23        | 1.00                 | 0.91                 | 1.2       | 275.4       | 0.003631       | 0.19           |
| -9.14       | 1.00                 | 0.34                 | 8.7       | 264.0       | 0.003788       | 2.16           |
| -19.21      | 1.00                 | 0.10                 | 1.0 x 10\(^2\) | 253.9 | 0.003938       | 4.61           |

Next, \( \ln(K_{eq}) \) was plotted versus \( 1/T \) to obtain the van’t Hoff plot (Figure S2). The equation of the line and associated errors were determined using the LINEST equation in Excel.
Figure S2. Plot of ln($K_{eq}$) versus $1/T$ (van’t Hoff plot) for complex 7.

Using the van’t Hoff equation, ln($K_{eq}$) = $-\Delta H^\circ / RT + \Delta S^\circ / R$ where $R = 8.3145 \times 10^{-3}$ kJ/mol·K, the enthalpy of reaction $\Delta H^\circ$ can be determined from the slope of the line in Figure S2 and the standard error in the slope (900 K, obtained from the LINEST equation):

$\Delta H^\circ = -1 \times \text{slope} \times R = -127 \pm 7$ kJ/mol

Similarly, the entropy of reaction $\Delta S^\circ$ can be determined from the intercept of the line in Figure S2 and the standard error in the intercept (3, obtained from the LINEST equation):

$\Delta S^\circ = \text{intercept} \times R = -0.46 \pm 0.03$ kJ/mol·K

Using the Gibbs free energy equation, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, the free energy can be calculated for $T = 298$ K to compare to the computed free energy for a reversible C–N bond forming step in Mg-catalyzed hydroamination. The calculated errors in $\Delta H^\circ$ and $\Delta S^\circ$ can be used and converting to kcal/mol gives the free energy:

$\Delta G^\circ = 2.5 \pm 0.3$ kJ/mol at 298 K; computed $\Delta G^\circ = 9.2$ kcal/mol at 298 K

This value compares more favourably to the computed free energy than does the free energy determined for complex 4 above, as both values show an endergonic process for C–N bond formation. However, C–N bond formation in the Mg system is still less favourable than in this Zr system.
Aza-Michael-Addition Mechanism

A plausible aza-Michael-addition mechanism for the addition of a secondary amine to 2-vinylpyridine to achieve a formal hydroamination, catalyzed by a Lewis acidic metal centre, can be seen below (Figure S3).

Figure S3. Plausible mechanism for aza-Michael-addition of secondary amines to 2-vinylpyridine.
NMR Spectra

**Figure S4.** $^1$H NMR spectrum of 4 (C$_6$D$_6$, 400 MHz, 298 K).

**Figure S5.** $^{13}$C NMR spectrum of 4 (C$_6$D$_6$, 100 MHz, 298 K).
Figure S6. $^1$H NMR spectrum of 5 (toluene-$d_8$, 400 MHz, 298 K).

Figure S7. $^{13}$C NMR spectrum of 5 (toluene-$d_8$, 100 MHz, 298 K).
Figure S8. $^1$H NMR spectrum of 6 (C$_6$D$_6$, 300 MHz, 298 K).

Figure S9. $^{13}$C NMR spectrum of 6 (C$_6$D$_6$, 75 MHz, 298 K).
Figure S10. $^1$H NMR spectrum of 8 (C$_6$D$_6$, 300 MHz, 298 K).

Figure S11. $^{13}$C NMR spectrum of 8 (C$_6$D$_6$, 75 MHz, 298 K).
Figure S12. $^1$H NMR spectrum of the hydroamination catalysis (toluene-$d_8$, 400 MHz, 298 K).$^6$

Figure S13. $^1$H NMR spectrum of 1 and 2-vinylpyridine (toluene-$d_8$, 400 MHz, 298 K).$^7$
**Figure S14.** $^1$H NMR spectrum of 6 and hydroamination product (toluene-$d_8$, 400 MHz, 298 K).

**Figure S15.** $^1$H NMR spectrum of 8 and 2-vinylpyridine (toluene-$d_8$, 300 MHz, 298 K).
Figure S16. $^1$H NMR spectrum of 7 and ferrocene (toluene-$d_8$, 400 MHz, 298 K).

Figure S17. $^1$H NMR spectrum of the hydroamination catalysis (toluene-$d_8$, 400 MHz, 298 K).
Figure S18. VT $^1$H NMR spectra of 7, olefinic region (400 MHz, toluene-$d_8$).
Figure S19. VT $^1$H NMR spectra of 4, olefinic region (400 MHz, toluene-$d_8$).

Crystallographic details
A summary of the crystallographic data for complexes 2, 4, 6, 7, and 8 is shown in Table S3. The automatic data collection strategy was determined using COSMO and the cell determination and integration processes were carried out using SAINT. Using Olex2,$^9$ the structures were solved with the ShelXT$^{10}$ structure solution program using Intrinsic Phasing and the structures were refined using the ShelXL$^{11}$ refinement package using the Least Squares method.

CCDC 1849489, 1849490, 1849491, 1849492, and 1849493 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
**Crystallographic tables:**

**Table S3.** List of crystallographic parameters for compounds 2, 4, 6, 7, and 8.

| Compound | 2 | 4 |
|----------|---|---|
| Empirical formula | C$_{33}$H$_{52}$N$_4$O$_2$Zr | C$_{30}$H$_{57}$N$_7$O$_2$Zr |
| Formula weight | 628.00 | 639.04 |
| Temperature/K | 90 | 100 |
| Crystal system | monoclinic | triclinic |
| Space group | P2$_1$/n | P-1 |
| a/Å | 11.411(2) | 11.0212(8) |
| b/Å | 20.388(4) | 11.6924(9) |
| c/Å | 14.842(3) | 14.0264(10) |
| α/° | 90 | 76.133(3) |
| β/° | 106.342(4) | 77.447(4) |
| γ/° | 90 | 80.581(4) |
| Volume/Å$^3$ | 3313.4(10) | 1701.0(2) |
| Z | 4 | 2 |
| ρ calc | 1.259 | 1.248 |
| μ/Å$^{-1}$ | 0.365 | 0.359 |
| F(000) | 1336.0 | 684.0 |
| Crystal size/mm$^3$ | 0.44 × 0.2 × 0.12 | 0.25 × 0.14 × 0.13 |
| Radiation | MoKα ($λ = 0.71073$) | MoKα ($λ = 0.71073$) |
| 2Θ range for data collection/° | 3.488 to 61.174 | 3.812 to 61.084 |
| Index ranges | -16 ≤ h ≤ 16, -29 ≤ k ≤ 29, -20 ≤ l ≤ 20 | -15 ≤ h ≤ 13, -16 ≤ k ≤ 16, -19 ≤ l ≤ 19 |
| Reflections collected | 38688 | 37732 |
| Independent reflections | 10051 [R$_{int}$ = 0.0401, R$_{sigma}$ = 0.0374] | 10263 [R$_{int}$ = 0.0299, R$_{sigma}$ = 0.0310] |
| Data/restraints/parameters | 10051/0/371 | 10263/0/375 |
| Goodness-of-fit on F$^2$ | 1.037 | 1.062 |
| Final R indexes [I≥2σ (I)] | R$_1$ = 0.0336, wR$_2$ = 0.0763 | R$_1$ = 0.0345, wR$_2$ = 0.0858 |
| Final R indexes [all data] | R$_1$ = 0.0454, wR$_2$ = 0.0813 | R$_1$ = 0.0404, wR$_2$ = 0.0886 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.88/-0.61 | 1.01/-0.41 |
| Compound | 6 | 7 |
|----------|---|---|
| Empirical formula | C$_{61}$H$_{116}$N$_{12}$O$_{4}$Zr$_{2}$ | C$_{34}$H$_{61}$N$_{7}$O$_{2}$Zr |
| Formula weight | 1264.09 | 691.11 |
| Temperature/K | 90 | 100 |
| Crystal system | triclinic | monoclinic |
| Space group | P-1 | P2$_1$/c |
| a/Å | 11.103(2) | 19.2374(14) |
| b/Å | 11.619(2) | 9.9154(8) |
| c/Å | 13.843(3) | 20.1776(14) |
| α/° | 80.868(4) | 90 |
| β/° | 66.762(4) | 109.871(4) |
| γ/° | 82.283(4) | 90 |
| Volume/Å$^3$ | 1615.2(5) | 3619.6(5) |
| Z | 1 | 4 |
| ρ calc g/cm$^3$ | 1.300 | 1.268 |
| μ/mm$^1$ | 0.376 | 0.343 |
| F(000) | 678.0 | 1480.0 |
| Crystal size/mm$^3$ | 0.14 × 0.07 × 0.04 | 0.32 × 0.21 × 0.16 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.224 to 56.018 | 4.114 to 60.906 |
| Index ranges | -14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -18 ≤ l ≤ 18 | -27 ≤ h ≤ 27, -14 ≤ k ≤ 10, -28 ≤ l ≤ 28 |
| Reflections collected | 29659 | 35882 |
| Independent reflections | 7777 [R$_\text{int}$ = 0.0570, R$_\text{sigma}$ = 0.0522] | 10890 [R$_\text{int}$ = 0.0392, R$_\text{sigma}$ = 0.0412] |
| Data/restraints/parameters | 7777/0/384 | 10890/0/407 |
| Goodness-of-fit on F$^2$ | 1.024 | 1.029 |
| Final R indexes [I≥2σ (I)] | R$_1$ = 0.0369, wR$_2$ = 0.0803 | R$_1$ = 0.0331, wR$_2$ = 0.0779 |
| Final R indexes [all data] | R$_1$ = 0.0499, wR$_2$ = 0.0855 | R$_1$ = 0.0424, wR$_2$ = 0.0823 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.97/-0.36 | 0.51/-0.39 |
| Property                        | Value                          |
|--------------------------------|--------------------------------|
| Compound                       | 8                              |
| Empirical formula              | C_{29}H_{58}N_{6}O_{2}Zr        |
| Formula weight                 | 614.03                         |
| Temperature/K                  | 100                            |
| Crystal system                 | monoclinic                     |
| Space group                    | P2\(\text{I}/c\)               |
| \(a/\text{Å}\)                 | 13.7581(7)                     |
| \(b/\text{Å}\)                 | 16.4217(8)                     |
| \(c/\text{Å}\)                 | 15.2414(8)                     |
| \(\alpha/\text{°}\)            | 90                             |
| \(\beta/\text{°}\)             | 100.6780(13)                   |
| \(\gamma/\text{°}\)            | 90                             |
| Volume/\(\text{Å}^3\)         | 3383.9(3)                      |
| \(Z\)                          | 4                              |
| \(\rho_{\text{calc}}\) g/cm\(^3\)| 1.205                          |
| \(\mu\) mm\(^{-1}\)          | 0.357                          |
| \(F(000)\)                     | 1320.0                         |
| Crystal size/mm\(^3\)         | 0.32 \times 0.11 \times 0.10  |
| Radiation                      | MoK\alpha (\(\lambda = 0.71073\)) |
| 2\(\theta\) range for data collection/\(\text{°}\)| 3.68 to 59.856 |
| Index ranges                   | -18 \(\leq h \leq 19\), -12 \(\leq k \leq 23\), -21 \(\leq l \leq 20\) |
| Reflections collected          | 38083                          |
| Independent reflections        | 9778 [\(R_{\text{int}} = 0.0418\), \(R_{\text{sigma}} = 0.0425\)] |
| Data/restraints/parameters     | 9778/0/353                     |
| Goodness-of-fit on \(F^2\)     | 1.055                          |
| Final R indexes [I\(\geq\)2\(\sigma\) (I)] | \(R_1 = 0.0382\), \(wR_2 = 0.0921\) |
| Final R indexes [all data]     | \(R_1 = 0.0521\), \(wR_2 = 0.0981\) |
| Largest diff. peak/hole / e \(\text{Å}^3\)| 1.13/-0.36 |
Figure S20. ORTEP representation of complex 2 with ellipsoids shown at 50% probability and hydrogen atoms omitted for clarity. Selected bond lengths: Zr1–C1, 2.3073(16) Å; Zr1–C8, 2.3017(16) Å; C1–C2, 1.482(2) Å; C9–C8, 1.484(2) Å. Selected bond angles: C2–C1–Zr1, 95.27(9)°; C9–C8–Zr1, 118.62(10)°; C8–Zr1–C1, 118.44(6)°. Selected atom distances: Zr1–C2, 2.8545(14) Å.
Figure S21. ORTEP representation of complex 6 with ellipsoids shown at 50% probability and hydrogen atoms and co-crystallized toluene omitted for clarity. Selected bond lengths: Zr1–N2, 2.1182(18) Å; Zr1–N1, 2.3398(17) Å; Zr1–N1*, 2.3644(18) Å. Selected bond angles: Zr1–N1–Zr1*, 104.05(6)°; N1*–Zr1–N2, 168.55(6)°; N1–Zr1–N2, 92.73(6)°. Selected sum of angles: N1, 321°; N2, 359°.
Figure S22. ORTEP representation of complex 7 with ellipsoids shown at 50% probability and hydrogen atoms omitted for clarity. Selected bond lengths: C1–C2, 1.363(2) Å; C2–C3, 1.430(2) Å; C3–C4, 1.360(2) Å; C4–C5, 1.460(2) Å; C5–C6, 1.369(2) Å; C6–C7, 1.494(2) Å; Zr1–N1, 2.3703(13) Å; Zr1–N2, 2.4250(12) Å; N2–C7, 1.5218(19) Å; N1–C5, 1.4149(19) Å; Zr1–N3, 2.0916(12) Å; N1–C1, 1.3757(19) Å; Selected bond angle: N1–Zr1–N3, 173.82(5)°.
Figure S23. ORTEP representation of complex 8 with ellipsoids shown at 50% probability and hydrogen atoms omitted for clarity. Selected bond lengths: Zr1−N2, 2.0775(15) Å; Zr1−N1, 2.0676(14) Å. Selected bond angles: N1−Zr1−N2, 117.67(6)°; C1−N1−Zr1, 126.04(10)°; C5−N1−Zr1, 122.74(11)°; C1−N1−C5, 111.22(13)°. Selected sum of angles: N1, 360°.
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