

Electronic Supplementary Information for:

Arrested Disproportionation in Trivalent, Mononuclear, and Non-Metallocene Complexes of Zr(III) and Hf(III).

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Experimental Section

General Procedures

Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified dinitrogen or using high vacuum standard Schlenk techniques under an argon or dinitrogen atmosphere. Hexanes, toluene, and tetrahydrofuran (THF) were purchased from Fisher Scientific and Et₂O was purchased from Sigma Aldrich. Solvents were sparged with argon for 20 minutes and dried using a two-column solvent purification system where the column designated for hexanes and toluene were packed with Q5 and alumina respectively, and the columns designated for Et₂O and THF were packed with alumina. Deuterated benzene was purchased from Cambridge Isotope Laboratories (CIL) and was sparged with nitrogen for 20 minutes, then was dried over a potassium mirror, vacuum transferred to a collection flask, and degassed by freeze–pump–thaw cycles. All solvents were transferred into a dry box and were stored over 4 Å sieves. All sieves were heated to 200 °C under vacuum overnight prior to use. Celite used for filtrations was also heated to 200 °C under vacuum overnight prior to use. ¹H NMR spectra were recorded on a Bruker AVIII 400 and AVII 500 MHz spectrometer, ¹³C NMR spectra were recorded on a Bruker AVII 500 MHz spectrometer, and ³¹P{¹H} spectra were recorded on a Bruker AVIII 400 spectrometer. ¹H NMR spectra are reported with reference to residual proteo solvent resonances of C₆D₆ at 7.16 ppm. ³¹P{¹H} NMR spectra were referenced to external H₃PO₄ (0 ppm). LiPN was prepared according to the published literature procedure.^[1] MCl₄(THF)₂ (M = Zr, Hf) were prepared by addition of THF into MCl₄ and recrystallized. Elemental analyses were measured by Midwest Microlab.

Synthesis of (PN)₂ZrCl₂ (1)

To a colorless suspension of solution of ZrCl₄(THF)₂ (543.5 mg, 1.44 mmol, 1 equiv.) in 3 mL toluene in a 20 mL vial was added a yellow 10 mL toluene solution of LiPN (1.00 g, 2.88 mmol, 2 eq.) while stirring at room temperature. After stirring for 12 hours, the reaction mixture turned bright orange, and a noticeable precipitate had formed, LiCl. The reaction mixture was filtered over Celite for removal of alkaline side product, and all volatiles were taken to dryness. The resulting orange oil was treated with hexane dropwise, while swirling the vial. Large orange crystals began to precipitate after swirling the oil and hexane mixture for one minute. After these initial crystals formed, they seeded the oil to form a large crystalline mass within another minute or less. The crystals were then triturated with hexanes to ensure removal of all toluene. The reaction has been confirmed by ¹H and ³¹P NMR to proceed in quantitative yields. The isolated crystalline solid is pure and can be used without further need for recrystallization (1.21 g, 1.44 mmol, 100%). To obtain crystals suitable for single crystal X-ray diffraction, 100 mg of the solid can be dissolved in a minimum of toluene (3 mL), layered with 5 mL of hexane, and stored at –35 °C overnight, resulting in the deposition of orange needles.

¹H NMR (400 MHz, C₆D₆, 298 K): δ 7.14-6.99 (m, unable to resolve *J* coupling value, 2H, C-*H*, Ar), 6.70 (d, *J*_{H-H} = 8.9 Hz, 2H, C-*H*, Ar), 6.57 (s, Δ*v*_{1/2} = 4.2 Hz, 4H, C-*H*, m-tolyl Ar), 5.56 (dd, *J*_{H-H} = 5.1, *J*_{P-H} = 8.5 Hz, 2H C-*H*, m-tolyl Ar), 2.61 (sept, ³*J*_{H-H} = 7.1 Hz, 4H, P-CHMe₂), 2.36 (s, Δ*v*_{1/2} = 3.7 Hz, 12H, CH₃, o-tolyl Ar), 2.16 (s, Δ*v*_{1/2} = 3.9 Hz, 6H, CH₃, p-Ar), 2.11 (s, Δ*v*_{1/2} = 4.2 Hz, 6H, CH₃, p-Ar), 1.38-1.51 (dd, two overlapping doublet of doublets, for one: ³*J*_{H-H} = 5.6 Hz, ³*J*_{P-H} = 13.0 Hz, for second, ³*J*_{H-H} = 7.7 Hz, ³*J*_{P-H} = 14.5 Hz, 24H, P-CHMe₂). ¹³C{¹H} NMR (125.8 MHz, C₆D₆, 298 K): 157.6 (d, *J*_{C-P} = 4.5 Hz, 2C, C-Ar), 157.4 (d, *J*_{C-P} = 4.4 Hz, 2C, C-Ar), 140.5

(4C, C-Ar), 136.8 (2C, C-Ar), 133.5 (d, $J_{C-P} = 2.2$ Hz, 2C, C-Ar), 132.9 (2C, C-Ar), 130.9 (4C, C-Ar), 122.2 (d, $J_{C-P} = 2.7$ Hz, 2C, C-Ar), 121.1 (d, $J_{C-P} = 2.5$ Hz, 2C, C-Ar), 115.1 (d, ${}^2J_{C-P} = 9.0$ Hz, 2C, C-Ar), 25.2 (d, $J_{C-P} = 8.2$ Hz, 4C, P-CHMe₂), 21.4 (2C, CH₃-Ar), 20.9 (d, ${}^2J_{C-P} = 2.0$ Hz, 4C, P-CHMe₂), 20.7 (4C, CH₃-Ar), 20.6 (d, ${}^2J_{C-P} = 2.4$, 4C, P-CHMe₂), 20.6 (2C, CH₃-Ar). ${}^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C₆D₆, 298 K): δ 11.44 (2P, Zr-P). Anal. Calcd for C₄₄H₆₂N₂P₂Cl₂Zr: C, 62.69; H, 7.41; N, 3.32. Found: C, 62.46; H, 7.32; N, 3.02.

Synthesis of (PN)₂HfCl₂ (2)

To a colorless suspension of solution of HfCl₄(THF)₂ (334.4 mg, 0.72 mmol, 1 equiv.) in 3 mL toluene in a 20 mL vial was added a yellow 10 mL toluene solution of LiPN (500 mg, 1.44 mmol, 2 eq.) while stirring at room temperature. After stirring for 12 hours, the reaction mixture turned darker yellow, and a noticeable precipitate had formed, LiCl. The reaction mixture was filtered over Celite for removal of alkaline side product, and all volatiles were taken to dryness. The resulting yellow oil was treated with hexane dropwise, while swirling the vial. Large yellow crystals began to precipitate after swirling the oil and hexane mixture for one minute. After these initial crystals formed, they seeded the oil to form a large crystalline mass within another minute or less. This solid is then dissolved in 1 mL of toluene and layered with 5 mL hexanes and stored at -35 °C overnight, resulting in the deposition of large yellow crystalline plates suitable for single crystal X-ray diffraction. (577.5 mg, 0.52 mmol, 72%).

${}^1\text{H}$ NMR (400 MHz, C₆D₆, 298 K): δ 7.14-6.99 (m, unable to resolve J coupling value, 2H, C-H, Ar), 6.73 (d, $J_{H-H} = 8.7$ Hz, 2H, C-H, Ar), 6.59 (s, $\Delta\nu_{1/2} = 4.4$ Hz, 4H, C-H, m-tolyl Ar), 5.63 (dd, $J_{H-H} = 5.1$, $J_{P-H} = 8.4$ Hz, 2H C-H, m-tolyl Ar), 2.66 (sept, ${}^3J_{H-H} = 7.0$ Hz, 4H, P-CHMe₂), 2.35 (s, $\Delta\nu_{1/2} = 3.8$ Hz, 12H, CH₃, o-tolyl Ar), 2.16 (s, $\Delta\nu_{1/2} = 4.7$ Hz, 6H, CH₃, p-Ar), 2.13 (s, $\Delta\nu_{1/2} = 4.6$ Hz, 6H, CH₃, p-Ar), 1.32-1.53 (dd, two overlapping doublet of doublets, for one: ${}^3J_{H-H} = 6.2$ Hz, ${}^3J_{P-H} = 13.2$ Hz, for second, ${}^3J_{H-H} = 3.3$ Hz, ${}^3J_{P-H} = 11.6$ Hz, 24H, P-CHMe₂). ${}^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, C₆D₆, 298 K): 157.6 (d, $J_{C-P} = 25.1$ Hz, 2C, C-Ar), 140.2 (4C, C-Ar), 136.2 (2C, C-Ar), 133.4 (2C, C-Ar), 133.0 (2C, C-Ar), 130.8 (4C, C-Ar), 119.9 (2C, C-Ar), 119.7 (2C, C-Ar), 116.2 (d, ${}^2J_{C-P} = 4.7$ Hz, 2C, C-Ar), 116.1 (d, ${}^2J_{C-P} = 4.3$ Hz, 2C, C-Ar), 26.2 (d, two overlapping doublets, unable to resolve J coupling, 4C, P-CHMe₂), 21.3 (CH₃-Ar), 20.7 (CH₃-Ar), 20.5 (CH₃-Ar), 20.9 (br, $\Delta\nu_{1/2} = 5.0$ Hz 8C, P-CHMe₂). ${}^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C₆D₆, 298 K): δ 8.76 (2P, Hf-P). Anal. Calcd for C₄₄H₆₂N₂P₂Cl₂Hf: C, 56.81; H, 6.72; N, 3.01. Found: C, 55.52; H, 6.69; N, 2.66.

Synthesis of (PN)₂ZrCl (3)

To an orange solution of **2** (100 mg, 0.12 mmol, 1 equiv.) in 2 mL THF in a 20 mL vial was added a 5 mL THF slurry of KC₈ (19.3 mg, 0.14 mmol, 1.2 eq.) while stirring. Both were chilled to -35 °C prior to addition. Immediately upon addition, a very distinct color change to red was observed. The mixture was then immediately filtered over Celite and taken to dryness. Due to the rapid disproportionation of **3** in polar solvents, the mixture must be kept cold (-196 °C in a coldwell is the preferred method) during this process. The residue was then dissolved in 5 mL hexanes and filtered once more to remove KCl. This solution was stored at -35 °C overnight, resulting in the deposition of a mixture of orange needles or **1** as well as large red crystalline plates. These crystals were suitable for single crystal X-ray diffraction, and were identified as **3** (25 mg, 0.03 mmol, 25.7%). Note that this yield is reported for the isolated crystals of **3**, which can be manually separated from **1**. Reported below are selected peaks from the paramagnetic ¹H NMR spectra (Figure S7) attributable to complex **3**. ¹H NMR (400 MHz, C₆D₆, 298 K): δ 12.30 (Δv_{1/2} = 14.0 Hz), 12.28 (Δv_{1/2} = 42 Hz), 11.10 (d, J = 8.0 Hz), 3.74 (d, J = 8.0 Hz). Anal. Calcd for C₄₄H₆₂N₂P₂Cl₂Hf: C, 65.44; H, 7.44; N, 3.47. Found: C, 65.08; H, 7.73; N, 3.14.

Synthesis of (PN)₂HfCl (4)

To a yellow solution of **2** (135 mg, 0.12 mmol, 1 equiv.) in 5 mL ether in a 20 mL vial was added a 5 mL ethereal slurry of KC₈ (20 mg, 0.13 mmol, 1.2 eq.) while stirring. Both were chilled to -35 °C prior to addition. Immediately upon addition, a very distinct color change to dark red was observed. The mixture was then immediately filtered over Celite and taken to dryness. Due to the rapid disproportionation of **3** in polar solvents, the mixture must be kept cold (-196 °C in a coldwell is the preferred method) during this process. The residue was then dissolved in 5 mL hexanes and filtered once more to remove KCl. This solution was stored at -35 °C overnight, resulting in the deposition of a mixture of yellow needles or **1** as well as large red crystalline plates. These crystals were suitable for single crystal X-ray diffraction, and were identified as **4**. Unfortunately, due to the much more rapid disproportionation of **4** compared to **3**, only a few crystals of **4** survive for single crystal X-ray diffraction. We are also able to collect EPR data in toluene as a glass. Reported below are selected peaks from the paramagnetic ¹H NMR spectra (Figure S8) attributable to complex **3**. ¹H NMR (400 MHz, C₆D₆, 298 K): δ 13.69 (Δv_{1/2} = 13.0 Hz), 11.80 (d, J = 8.0 Hz), 4.34 (d, J = 8.0 Hz). Attempts to obtain satisfactory combustion analysis failed due to the thermal sensitivity of the compound.

NMR Spectral Data

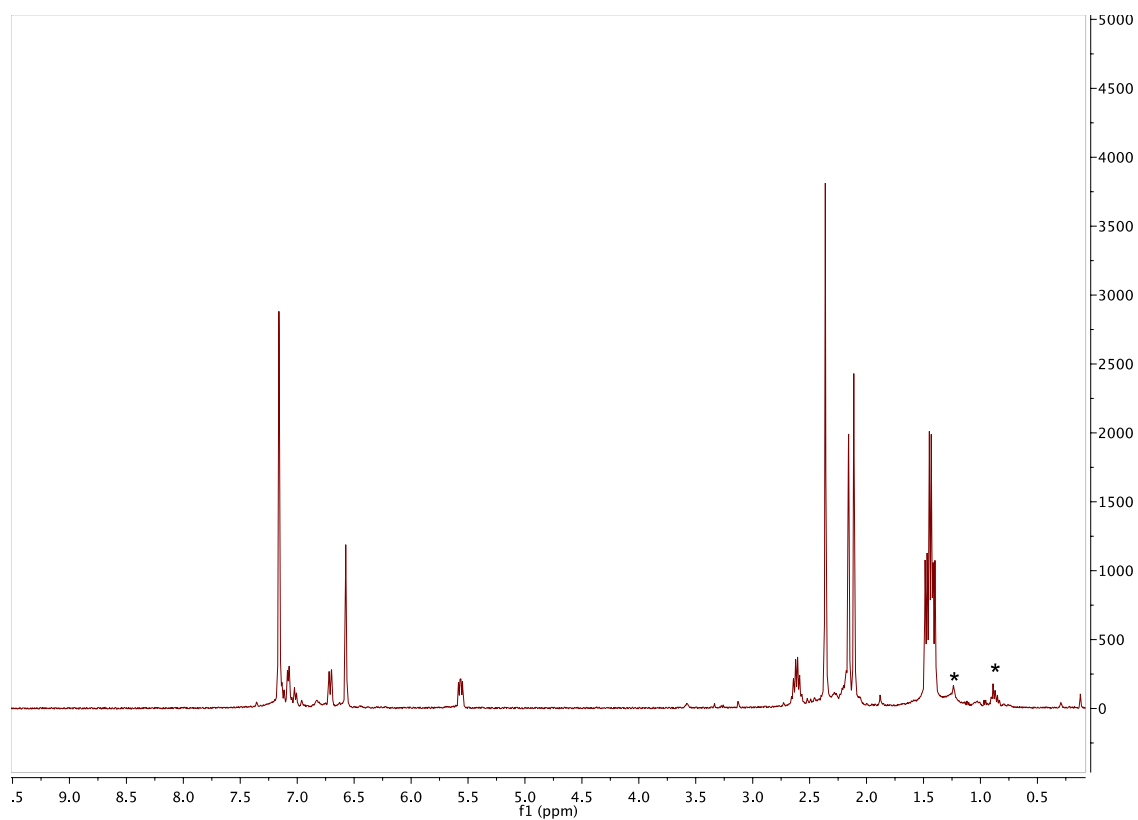


Figure S1: ^1H NMR Spectrum of **1** in C_6D_6 , 400 MHz, 298 K, * denotes residual hexane.

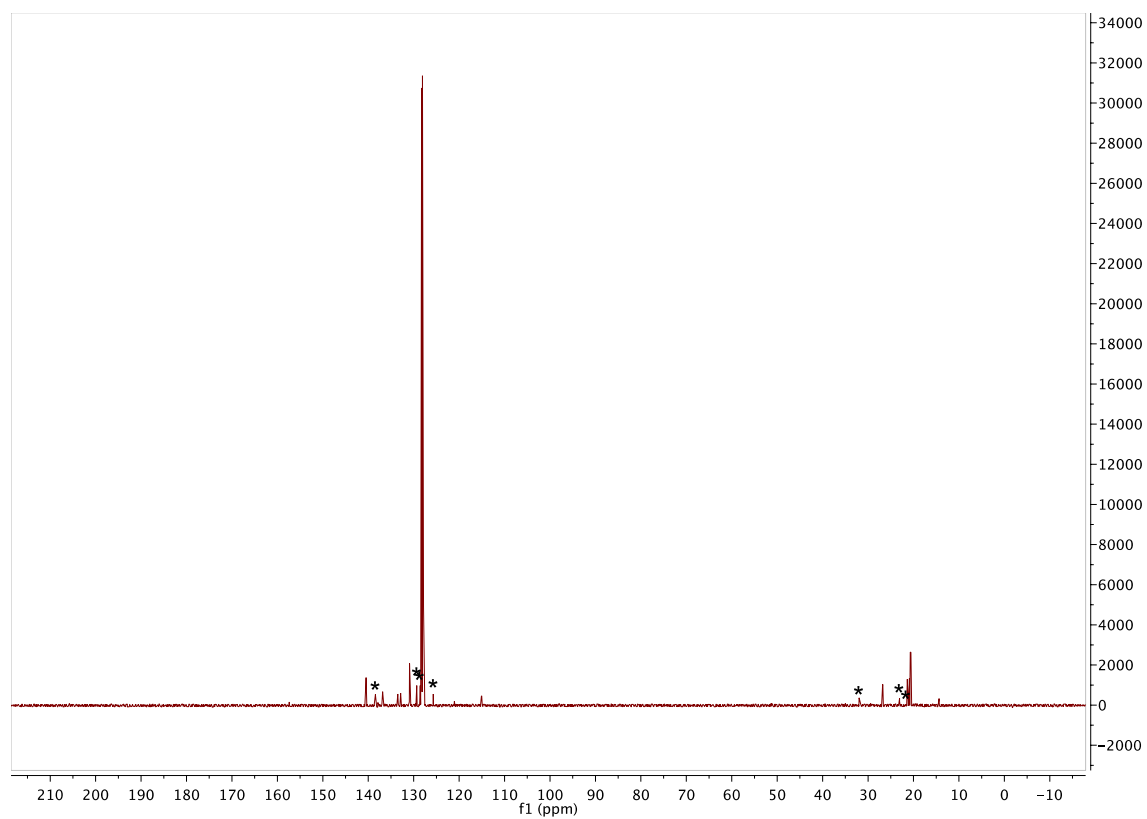


Figure S2: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **1** in C_6D_6 , 125.8 MHz, 298 K, * denotes residual hexane and toluene.

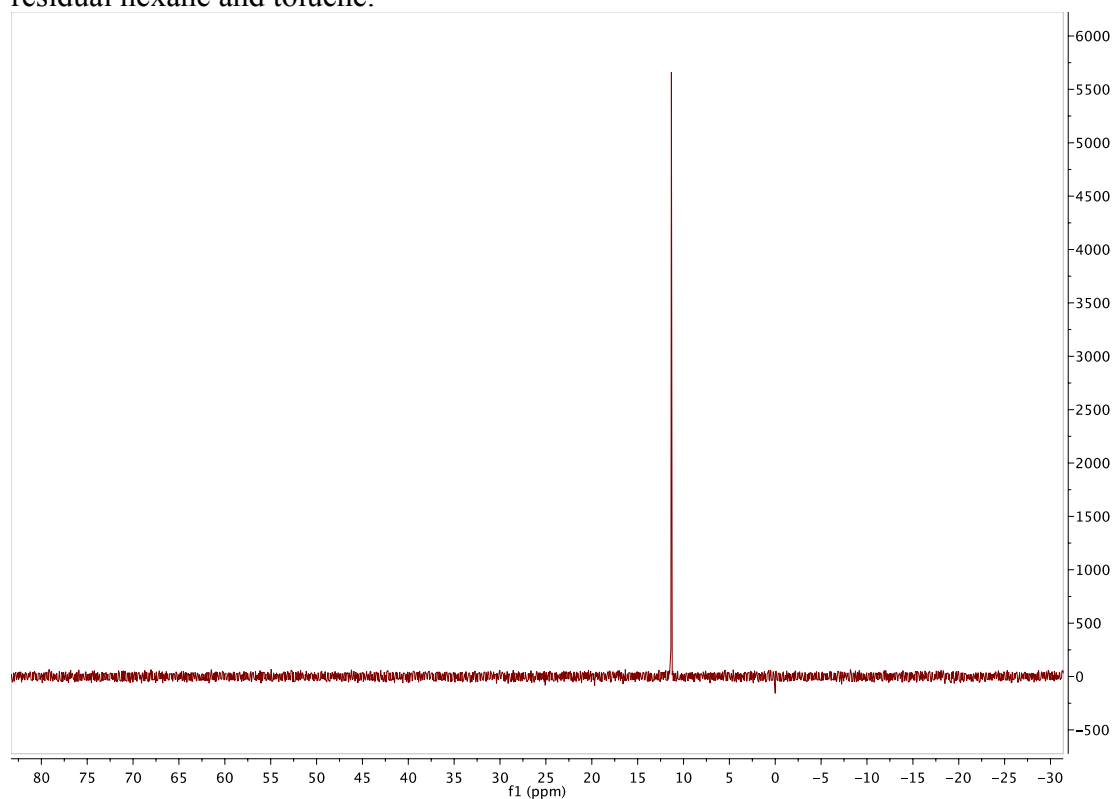


Figure S3: $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of **1** in C_6D_6 , 162 MHz, 298 K

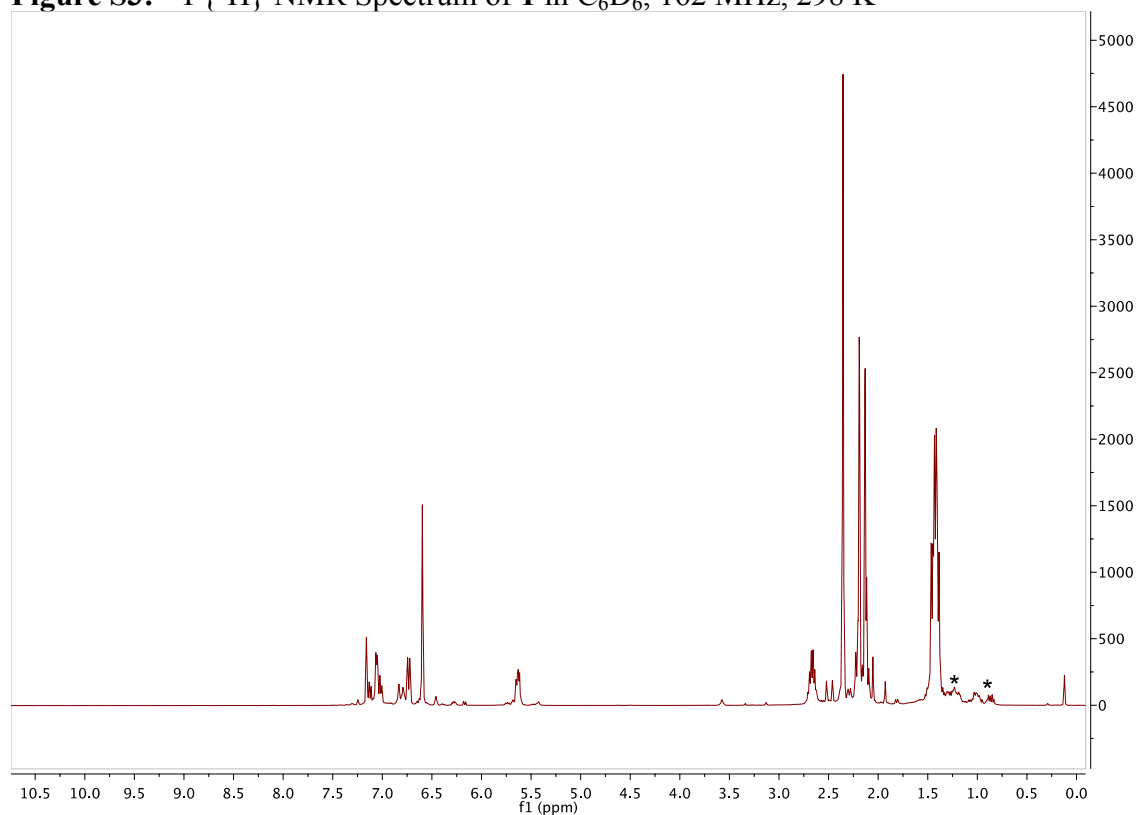


Figure S4: ^1H NMR Spectrum of **2** in C_6D_6 , 400 MHz, 298 K

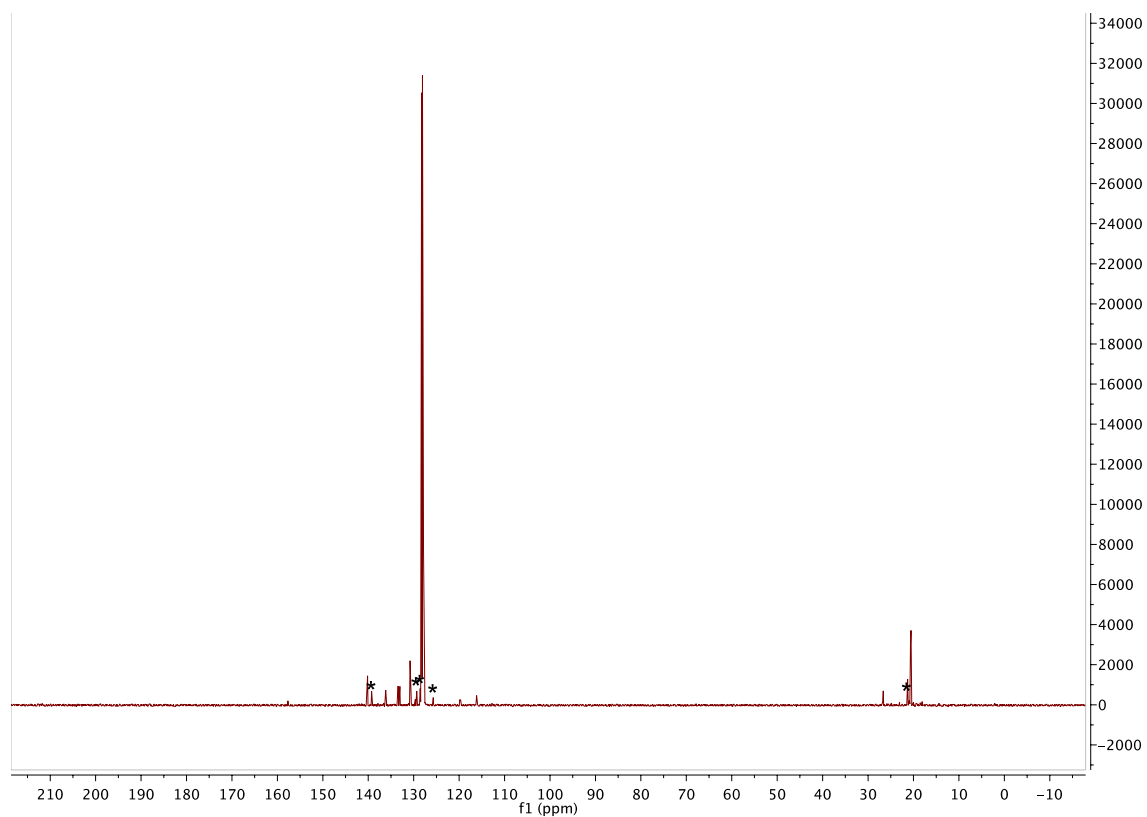


Figure S5: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2** in C_6D_6 , 125.8 MHz, 298 K, * denotes residual toluene.

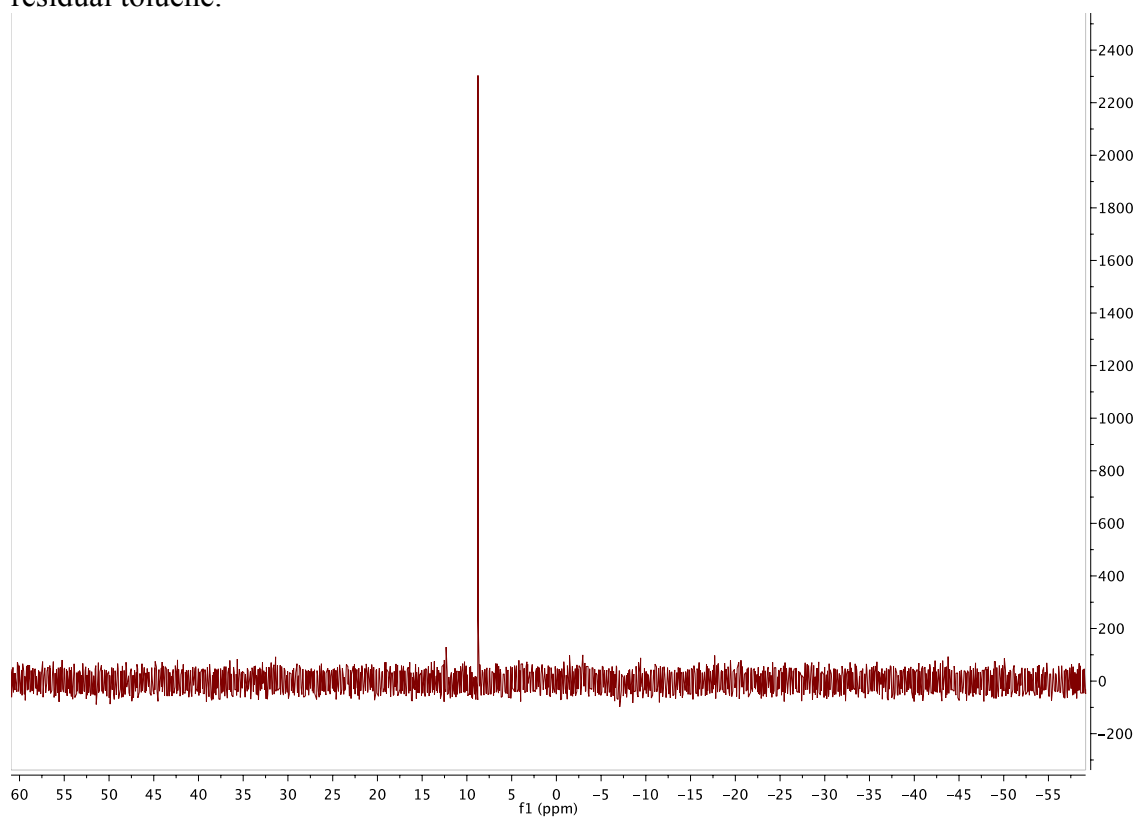


Figure S6: $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of **2** in C_6D_6 , 162 MHz, 298 K

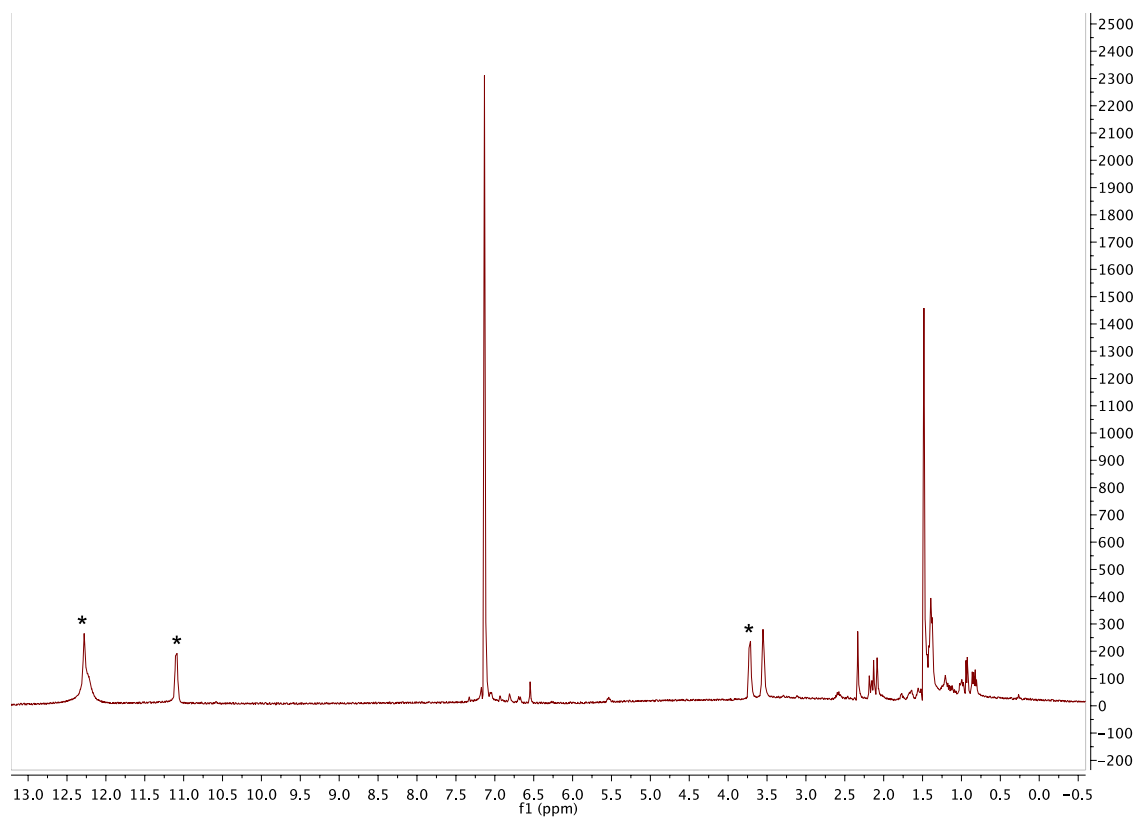


Figure S7: ^1H NMR Spectrum of **3** in C_6D_6 with **1** from disproportionation, 400 MHz, 298 K. * denote peaks that are inconclusively attributable to **3**.

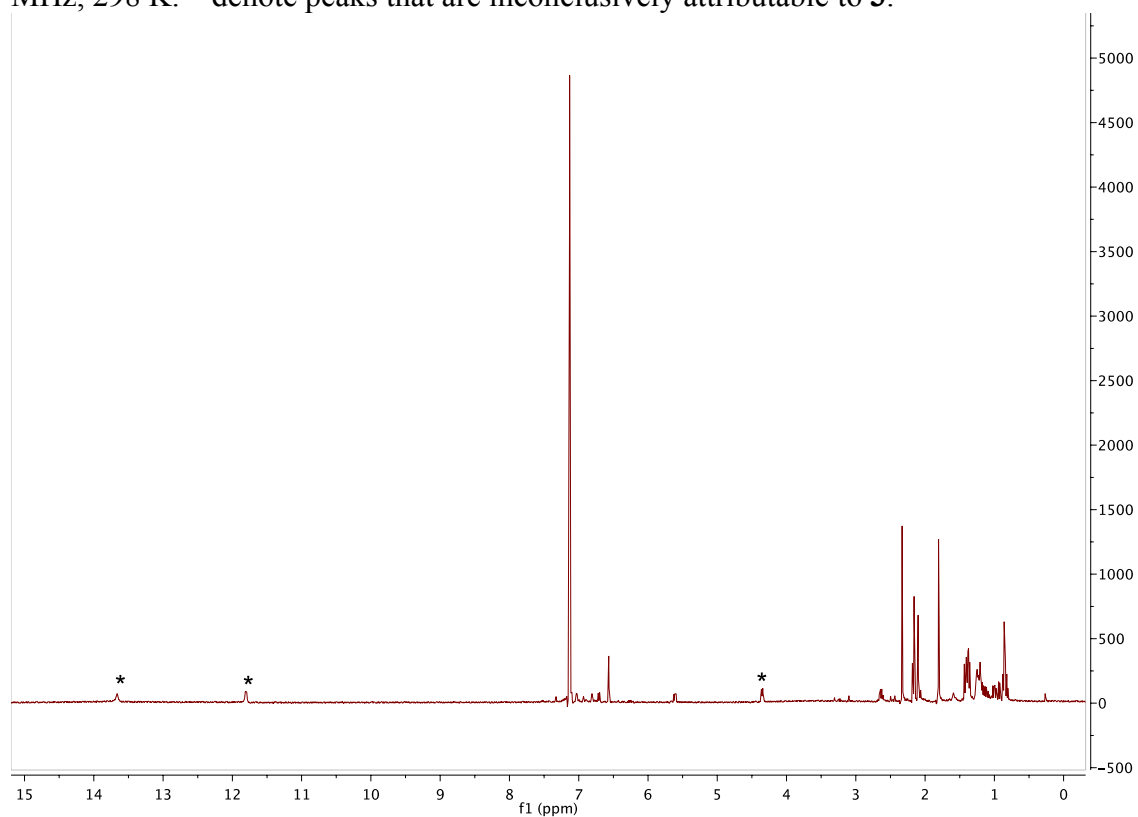


Figure S8: ^1H NMR Spectrum of **4** in C_6D_6 with **2** from disproportionation, 400 MHz, 298 K. * denote peaks that are inconclusively attributable to **4**.

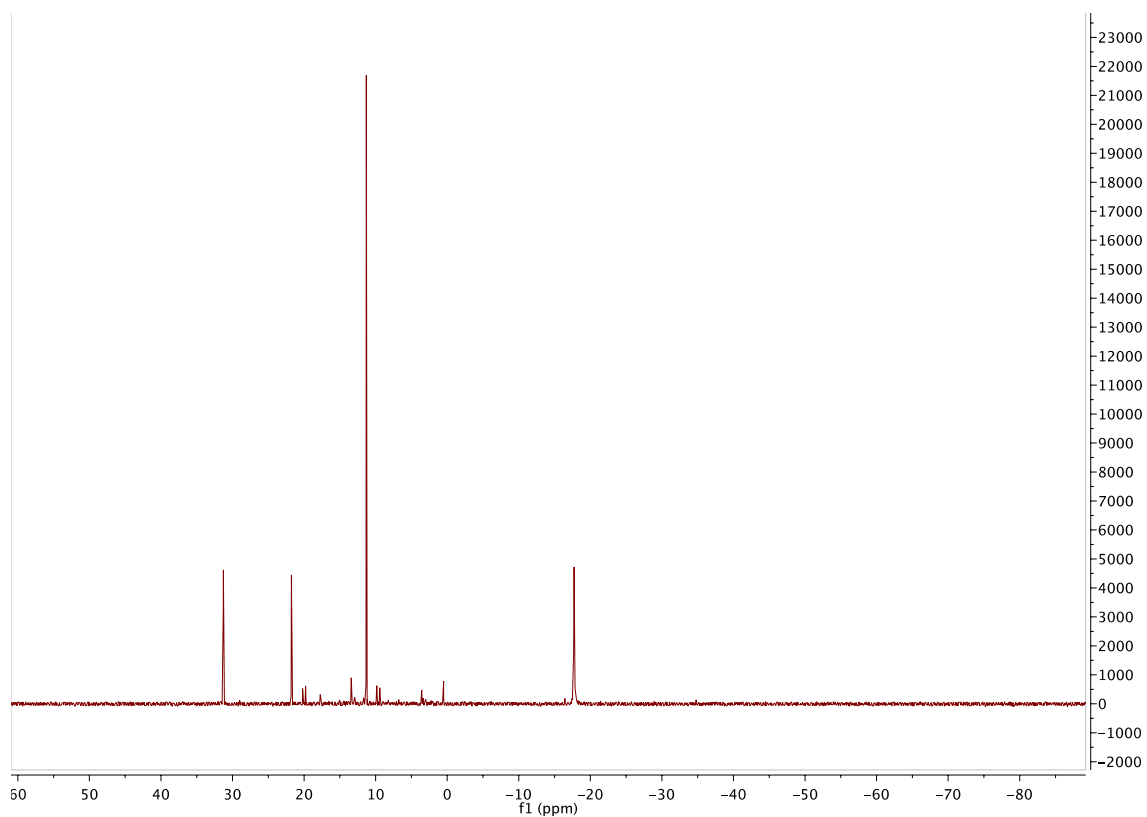


Figure S9: $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of crude reaction mixture of **3** in C_6D_6 , 162 MHz, 298 K.

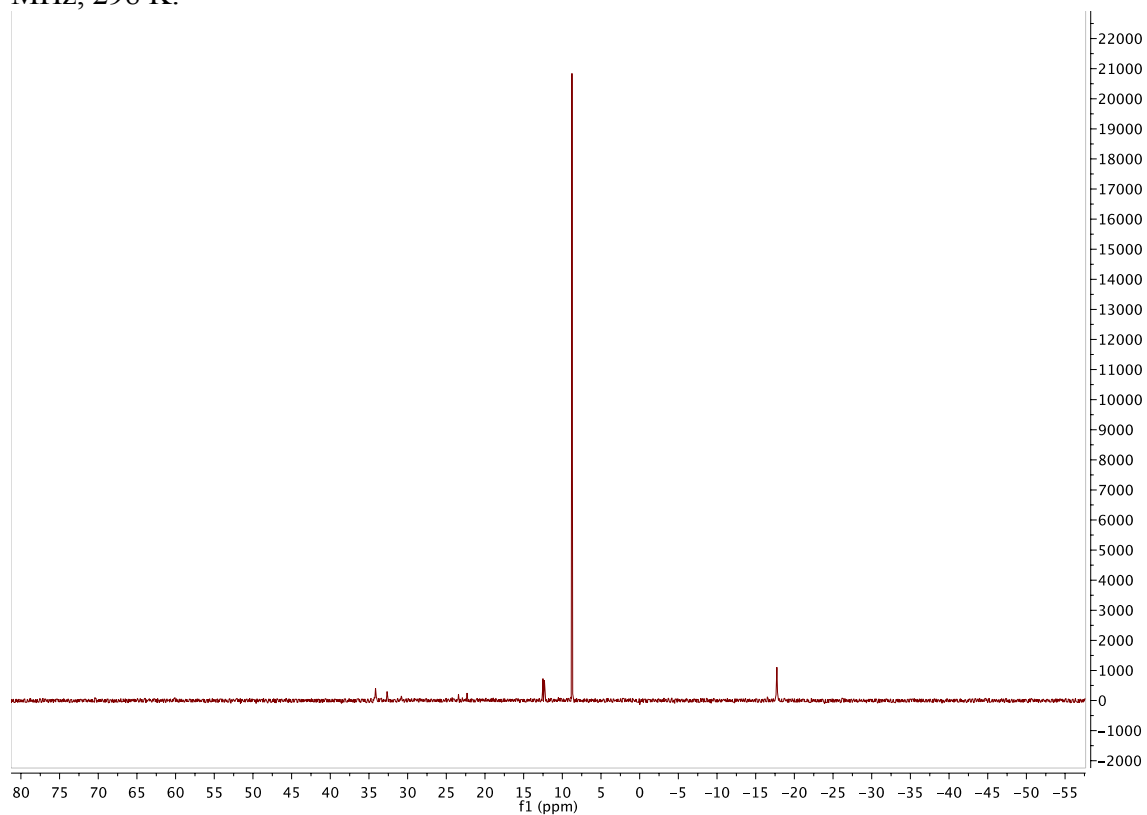


Figure S10: $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of crude reaction mixture of **4** in C_6D_6 , 162 MHz, 298 K.

Crystallographic Experimental Details

Crystallographic data are summarized Table S1-S4. Suitable crystals for X-ray analysis of **1-4** were placed on the end of a Cryoloop coated in NVH oil. Data for single crystal structure determination of **1** and **4** were taken on a Bruker ApexII with a CCD, while **2** and **3** were taken on a Bruker D8 with CMOS area detector employing graphite-monochromated Mo-K α radiation ($\lambda=0.71073$ Å) at a temperature of 100(1) K. Rotation frames were integrated using SAINT,^[2] producing a list of non-averaged F^2 and $\sigma(F^2)$ values. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.^[3] The initial structure of **1** was solved by direct methods – SIR2004.^[4] The initial structure of **2** was solved by direct methods – SHELXS.^[5] The initial structures of **3** and **4** were solved by dual methods – SHELXT.^[5] Refinement was by full-matrix least squares based on F^2 using SHELXL-2014.^[6] All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined with riding models. These results were checked using the IUCR's CheckCIF routine. The alerts in the output are related to the co-crystallized solvents.

For **1**, two sites occupied by hexane molecules were identified in the asymmetric unit. These sites were considerably disordered and were treated by SQUEEZE as a diffuse contribution.^[7] In the resulting void space, a contribution of 881 e⁻ per unit cell was found and taken to represent two hexane molecules in the asymmetric unit.

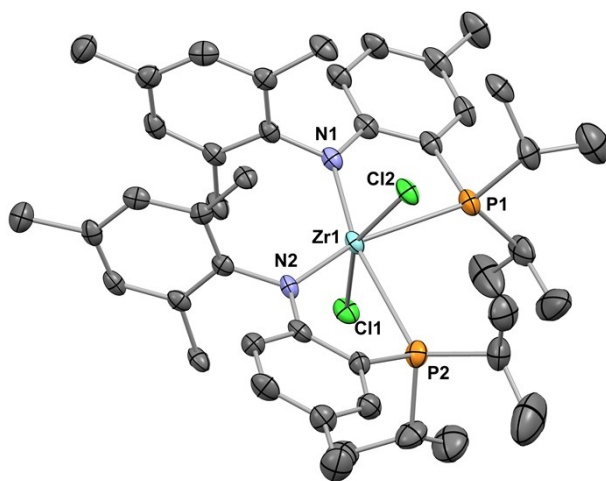


Figure S11. Molecular structure of complex **1**, showing thermal ellipsoids at the 50% probability level. Hydrogens have been omitted for clarity.

Table S1. Crystallographic Data for 1 · hexane

Molecular formula	C ₄₄ H ₆₂ Cl ₂ N ₂ P ₂ Zr, (C ₆ H ₁₄)
Formula weight	1015.35
Temperature (K)	100(1)
Crystal system	<i>Orthorhombic</i>
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Cell constants:	
a (Å)	13.3448(6)

b (Å)	25.7942(13)
c (Å)	31.7835(15)
Alpha Angle	90
Beta Angle	90
Gamma Angle	90
Volume (Å ³)	10940.5(9)
Z	8
Density (calcd mg/m ³)	1.233
Abs coeff (mm ⁻¹)	0.394
F(000)	4352
Wavelength	0.71073
θ range for data collection (°)	1.993 to 27.562
<i>h, k, l</i> ranges collected	-17 ≤ <i>h</i> ≤ 17 -33 ≤ <i>k</i> ≤ 33 -41 ≤ <i>l</i> ≤ 41
# Reflns collected	168592
Refinement method	Full-matrix least-squares on F ²
<i>R</i> ₁ ^a	0.0393
<i>wR</i> ₂ ^b	0.0844
Goodness-of-fit on F ^{2c}	1.025
Flack Parameter	-0.004(10)

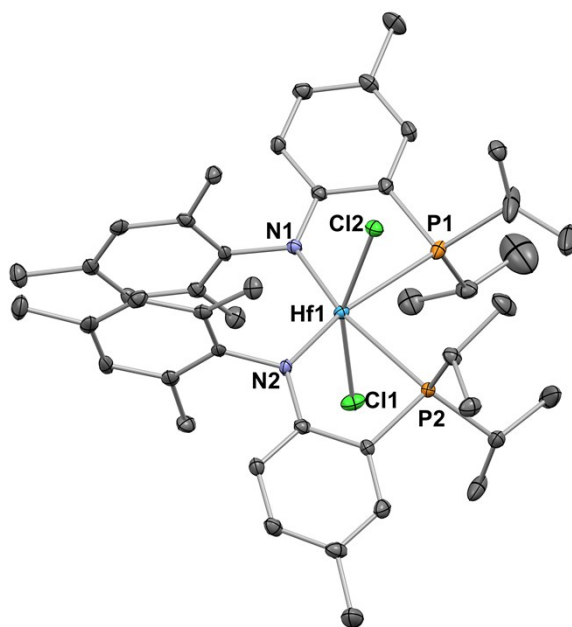


Figure S12. Molecular structure of **2**, showing thermal ellipsoids at 50% probability level. Hydrogens have been omitted for clarity.

Table S2. Crystallographic Data for **2** · toluene

Molecular formula	C ₄₄ H ₆₂ Cl ₂ Hf N ₂
Formula weight	1114.55
Temperature (K)	100(1)
Crystal system	<i>Orthorhombic</i>
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Cell constants:	
a (Å)	13.3358(6)
b (Å)	25.5782(13)
c (Å)	31.8420(14)
Alpha Angle	90
Beta Angle	90
Gamma Angle	90
Volume (Å ³)	10861.5(9)
Z	8
Density (calcd mg/m ³)	1.363
Abs coeff (mm ⁻¹)	2.116
F(000)	4608
Wavelength	0.71073
θ range for data collection (°)	2.836 to 27.551
	-17 ≤ h ≤ 17
<i>h, k, l</i> ranges collected	-33 ≤ k ≤ 33
	-41 ≤ l ≤ 37
# Reflns collected	190735
Refinement method	Full-matrix least-squares on F ²
<i>R</i> ₁ ^a	0.0248
<i>wR</i> ₂ ^b	0.0617
Goodness-of-fit on <i>F</i> ^{2c}	1.058
Flack Parameter	-0.0105(11)

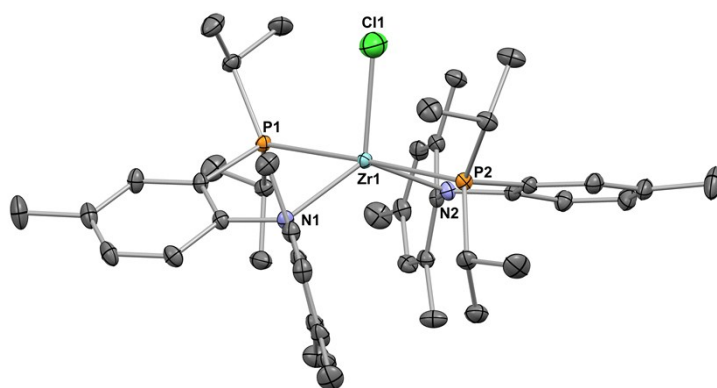


Figure S13. Molecular structure of **3**, showing thermal ellipsoids at 50% probability level. Hydrogens have been omitted for clarity.

Table S3. Crystallographic Data for 3

Molecular formula	C ₄₄ H ₆₂ Cl N ₂ P ₂ Zr
Formula weight	807.56
Temperature (K)	100(1)
Crystal system	<i>Monoclinic</i>
Space group	<i>P 1 21/n 1</i>
Cell constants:	
a (Å)	17.7014(6)
b (Å)	13.7831(5)
c (Å)	17.8222(7)
Alpha Angle	90
Beta Angle	99.9610(10)
Gamma Angle	90
Volume (Å ³)	4282.7(3)
Z	4
Density (calcd mg/m ³)	1.252
Abs coeff (mm ⁻¹)	0.425
F(000)	1708
Wavelength	0.71073
θ range for data collection (°)	2.956 to 27.568
<i>h, k, l</i> ranges collected	-23 ≤ <i>h</i> ≤ 23 -17 ≤ <i>k</i> ≤ 17 -22 ≤ <i>l</i> ≤ 23
# Reflns collected	94375
Refinement method	Full-matrix least-squares on F ²
<i>R</i> ₁ ^a	0.0356
<i>wR</i> ₂ ^b	0.0978
Goodness-of-fit on F ^{2c}	1.099

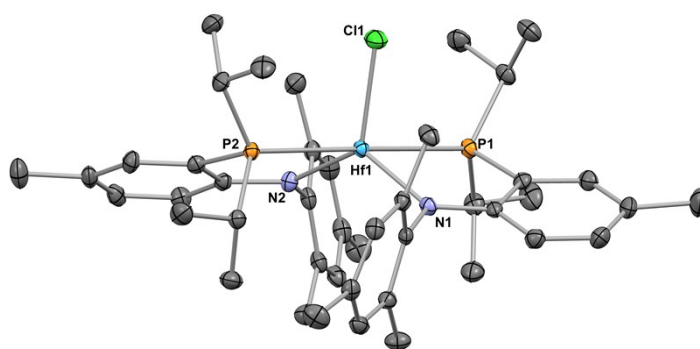


Figure S14. Molecular structure of **3**, showing thermal ellipsoids at 50% probability level. Hydrogens have been omitted for clarity.

Table S4. Crystallographic Data for 4

Molecular formula	C ₄₄ H ₆₂ Cl Hf N ₂ P ₂
Formula weight	894.83
Temperature (K)	100(1)

Crystal system	<i>Monoclinic</i>
Space group	<i>P 1 21/n 1</i>
Cell constants:	
a (Å)	17.7270(5)
b (Å)	13.7111(4)
c (Å)	17.8490(5)
Alpha Angle	90
Beta Angle	99.7730(10)
Gamma Angle	90
Volume (Å ³)	4275.4(2)
Z	4
Density (calcd mg/m ³)	1.390
Abs coeff (mm ⁻¹)	2.609
F(000)	1836
Wavelength	0.71073
θ range for data collection (°)	2.956 to 27.568
<i>h, k, l</i> ranges collected	-23 ≤ <i>h</i> ≤ 23 -17 ≤ <i>k</i> ≤ 17 -23 ≤ <i>l</i> ≤ 23
# Reflns collected	79238
Refinement method	Full-matrix least-squares on F ²
<i>R</i> ₁ ^a	0.0232
<i>wR</i> ₂ ^b	0.0483
Goodness-of-fit on <i>F</i> ^{2c}	1.051

^a $R_1 = (|F_o| - |F_c|) / |F_o|$. ^b $wR_2 = \sqrt{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]}$. ^c Goodness-of-fit = $\sqrt{[\sum w(F_o^2 - F_c^2)^2 / (N_{\text{observns}} - N_{\text{params}})]}$, all data.

Electron Paramagnetic Resonance (EPR) Experimental Details

EPR spectra were recorded on a JEOL continuous wave spectrometer JES-FA200 equipped with an X-band Gunn oscillator bridge, a cylindrical mode cavity, and a helium cryostat. The samples were freshly dissolved in the respective solvent in an air-tight quartz EPR tube under nitrogen atmosphere in the glovebox. The solutions in the tube were frozen in liquid nitrogen upon exiting the glovebox and kept frozen until measured. Analysis and simulation of the data was done using the software “eview” and “esim” written by E. Bill (mail: ebill@gwdg.de, MPI for Chemical Energy Conversion, Mülheim an der Ruhr).

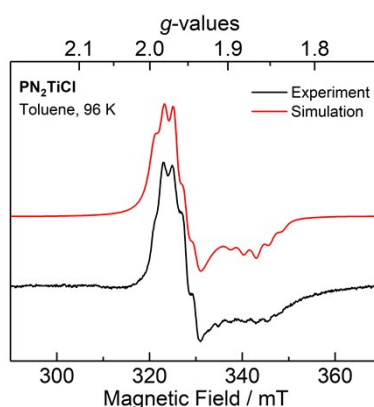


Figure S15: CW X-band EPR spectra of $(\text{PN})_2\text{TiCl}$ at 96 K, recorded in ~ 1 mM frozen solution in toluene (black trace), and its simulation (red trace). Experimental conditions: microwave frequency $\nu = 8.959$ GHz, modulation width = 0.4 mT, microwave power = 1.0 mW, modulation frequency = 100 kHz, time constant = 0.1 s. Simulation parameters: effective spin $S = 1/2$, effective g-values $g_1 = 1.97$, $g_2 = 1.97$, $g_3 = 1.87$, line widths $W_1 = 1.8$ mT, $W_2 = 1.8$ mT, $W_3 = 1.5$ mT, and super hyperfine coupling to two nitrogen nuclei (^{14}N , $I = 1$, 99.6 %) of $A_1 = 2.10$ mT (56.9 MHz), $A_2 = 2.10$ mT (56.9 MHz), $A_3 = 2.66$ mT (71.9 MHz).

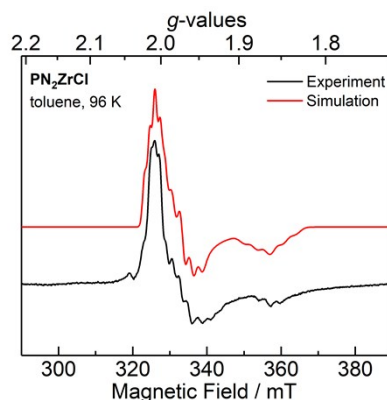


Figure S16: CW X-band EPR spectra of **3** at 96 K, recorded in ~ 1 mM frozen solution in toluene (black trace), and its simulation (red trace). Experimental conditions: microwave frequency $\nu = 8.956$ GHz, modulation width = 0.4 mT, microwave power = 1.0 mW, modulation frequency = 100 kHz, time constant = 0.1 s. Simulation

parameters: effective spin $S = 1/2$, effective g-values $g_1 = 1.96$, $g_2 = 1.92$, $g_3 = 1.79$, line widths $W_1 = 1.1$ mT, $W_2 = 1.7$ mT, $W_3 = 2.8$ mT, and super hyperfine coupling to two nitrogen nuclei (^{14}N , $I = 1$, 99.6 %) of $A_1 = 1.33$ mT (35.9 MHz), $A_2 = 2.22$ mT (59.9 MHz), $A_3 = 3.10$ mT (83.9 MHz).

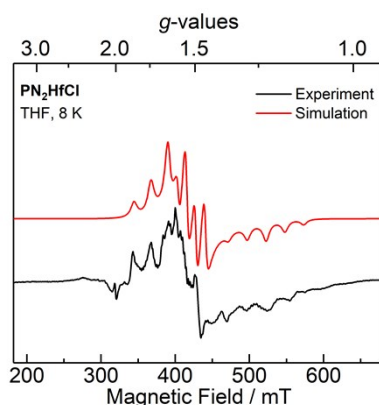


Figure S17: CW X-band EPR spectra of **4** at 8 K, recorded in 1 mM frozen solution in THF (black trace), and its simulation (red trace). Experimental conditions: microwave frequency $\nu = 8.961$ GHz, modulation width = 0.4 mT, microwave power = 1.0 mW, modulation frequency = 100 kHz, time constant = 0.1 s. Simulation parameters: effective spin $S = 1/2$, effective g-values $g_1 = 1.64$, $g_2 = 1.54$, $g_3 = 1.23$, line widths of $W_1 = 6.0$ mT, $W_2 = 3.9$ mT, $W_3 = 6.0$ mT, and super hyperfine coupling to two nitrogen nuclei (^{14}N , $I = 1$, 99.6 %) of $A_1 = 19.4$ mT (524 MHz), $A_2 = 9.41$ mT (255 MHz), $A_3 = 16.1$ mT (435 MHz).

References

- [1] B. L. Tran, M. Pink and D. J. Mindiola, *Organometallics*, 2009, **28**, 2234-2243.
- [2] SAINT; Bruker AXS Inc.: Madison, WI, USA. 2009.
- [3] G. M. Sheldrick, *SADABS*; University of Gottingen: Germany, 2007.
- [4] M. C. Burla, R. Caliendo, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidoria and R. Spagna, *J. Appl. Cryst.*, 2005, **38**, 381.
- [5] G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3.
- [6] G. M. Sheldrick, "Crystal Structure Refinement with SHELXL" *Acta Crystallogr.*, **2015**, *C71*, 3.
- [7] (a) P. van der Sluis and A. L. Spek, *Acta Crystallogr.*, 1990, **A46**, 194. (b) A. L. Spek, *Acta Crystallogr.*, 2009, **D65**, 148. (c) A. L. Spek, *Acta Crystallogr.*, 2015, **C71**, 9.