Electronic Supplementary Material (ESI) for Chemical Communications
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# N-H Activation of Hydrazines by a Heterobimetallic Zr-Co Complex: Promotion of One-electron Chemistry at Zr

**SUPPORTING INFORMATION**

***J.W. Napoline, Mark W. Bezpalko, Bruce M. Foxman, Christine M. Thomas****

**CONTENTS**

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## Experimental Section

**General Considerations.** All syntheses reported were carried out using standard glovebox and Schlenk techniques in the absence of water and dioxygen, unless otherwise noted. Benzene, pentane, diethyl ether, tetrahydrofuran, and toluene were degassed and dried by sparging with $N_2$ gas followed by passage through an activated alumina column. All solvents were stored over 3 Å molecular sieves. Deuterated benzene was purchased from Cambridge Isotope Laboratories, Inc., degassed via repeated freeze-pump-thaw cycles, and dried over 3 Å molecular sieves. Solvents were frequently tested using a standard solution of sodium benzophenone ketyl in tetrahydrofuran to confirm the absence of oxygen and moisture. (THF)Zr(MesNP$^i$Pr$_2$)$_3$CoN$_2$ (**1**) was synthesized using literature procedures.[1] All other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were recorded at ambient temperature on a Varian Inova 400 MHz instrument. $^1$H NMR chemical shifts were referenced to residual solvent. IR spectra were recorded on a Varian 640-IR spectrometer controlled by Resolutions Pro software. UV-vis spectra were recorded on a Cary 50 UV-vis spectrophotometer using Cary WinUV software. Elemental microanalyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

**X-ray Crystallography Procedures.** All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite monochromated Mo Kα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[2] Preliminary cell constants were obtained from three sets of 12 frames. Fully labeled diagrams and data collection and refinement details are included in Table S1 and on pages S8-S16 of the Supporting Information file. Further crystallographic details may be found in the CIF files deposited in the CCDC (892502-892504).

**Electrochemistry**. Cyclic voltammetry measurements were carried out in a glovebox under a dinitrogen atmosphere in a one-compartment cell using a CH Instruments electrochemical analyzer. A glassy carbon electrode and platinum wire were used as the working and auxiliary electrodes, respectively. The reference electrode was Ag/AgNO$_3$ in THF. Solutions (THF) of electrolyte (0.40 M [$^n$Bu$_4$N][PF$_6$]) and analyte (2 mM) were also prepared in the glovebox. Cyclic voltammograms shown in Figures S7-S9 are the result of the first scan measured for each compound.

[1] Greenwood, B. P.; Rowe, G. T.; Chen, C.-H.; Foxman, B. M.; Thomas, C. M. *J. Am. Chem. Soc.* **2010**, *132*, 44-45.
[2] Apex2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, June 2006.

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**Computational Details.** All calculations were performed using Gaussian09, Revision A.02 for the Linux operating system.[3] Density functional theory calculations were carried out using a combination of Becke's 1988 gradient-corrected exchange functional[4] and Perdew's 1986 electron correlation functional[5] (BP86). A mixed-basis set was employed, using the LANL2TZ(f) triple zeta basis set with effective core potentials for cobalt and zirconium,[6] Gaussian09's internal 6-311+G(d) for heteroatoms (nitrogen, oxygen, phosphorus), and Gaussian09's internal LANL2DZ basis set (equivalent to D95V[7]) for carbon and hydrogen. Using crystallographically determined geometries as a starting point, the geometries were optimized to a minimum, followed by analytical frequency calculations to conform that no imaginary frequencies were present.

**($\eta^2$-NHNH$_2$)Zr(MesNP$^i$Pr$_2$)$_3$CoN$_2$ (2)**

A solution of hydrazine (1.8 μL, 0.056 mmol) in $C_6H_6$ (1 mL) was layered onto a frozen solution of **1** (0.0375 g, 0.0375 mmol) in $C_6H_6$ (7 mL). The reaction mixture was warmed to room temperature and stirred for 30 min. The resulting yellow/orange solution was filtered through Celite, and the volatiles were removed from the filtrate in vacuo to yield a yellow/orange residue. The resulting residue was washed with cold (-35°C) *n*-pentane (4 mL) to yield analytically pure product as a yellow powder (0.029 g, 0.030 mmol, 80.6%). Crystals suitable for X-ray diffraction were grown from a concentrated diethyl ether solution at -35°C. $^1$H NMR (400 MHz, $C_6D_6$): δ 7.7 (s, 6H, H-Ar), 5.55 (bs, 18H, CH(C*H*$_3$)$_2$), 2.86 (bs, 2H, NH$_2$), 2.65 (s, 18H CH(C*H*$_3$)$_2$), 2.23 (s, 9H, *p*-Me-Ar), -1.94 (bs, 18H, *o*-Me -Ar), -20.17 (bs, 1H, NH) (not observed; C*H*(CH$_3$)$_2$). UV-vis ($C_6H_6$ , λ(nm) (ε, M$^{-1}$cm$^{-1}$)): 341 (2.0 x 10$^3$), 456 (450), 507 (260), 613 (140), 674 (140). Evans' method ($C_6D_6$): 2.00 μB. IR ($C_6H_6$): 2043 cm$^{-1}$ (Co-N$_2$). Anal. Calcd for $C_{45}H_{78}N_7P_3CoZr$: C, 56.29; H, 8.19; N, 10.21. Found: C, 56.11; H, 8.24; N, 10.14.

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[3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
[4] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
[5] Perdew, J. P. *Physical Review B* **1986**, *33*, 8822.
[6] (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299-310. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299-310. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299-310. (d) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270-283.
[7] Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York,
1976; Vol. 3, p 1-28.

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**($\eta^2$-$MeN_2H_3$)Zr($MesNP^iPr_2$)$_3$$CoN_2$ (3)**

A solution of methylhydrazine (3.0 μL, 0.056 mmol) in $C_6H_6$ (1 mL) was layered onto a frozen solution of **1** (0.0375 g, 0.0375 mmol) in $C_6H_6$ (7 mL). The reaction mixture was warmed to room temperature and stirred for 30 min. The resulting yellow/orange solution was filtered through Celite, and the volatiles were removed from the filtrate in vacuo to yield a yellow/orange residue. The resulting residue was washed with cold (-35°C) *n*-pentane (4 mL) to yield analytically pure product as a yellow powder (0.031 g, 0.032 mmol, 84.9%). Crystals suitable for X-ray diffraction were grown from a concentrated diethyl ether solution at -35°C. $^1$H NMR (400 MHz, $C_6D_6$): δ, 7.73 (s, 6H, H-Ar), 5.62 (bs, 18H, CH(C$H_3$)$_2$), 3.61 (s, 3H, Me-N), 2.64 (s, 18H, CH(C$H_3$)$_2$), 2.35 (bs, 2H, $NH_2$), 2.20 (s, 9H, *p*-Me-Ar), -1.89 (bs, 18H, *o*-Me -Ar), (Not observed; C*H*($CH_3$)$_2$). UV-vis ($C_6H_6$ , λ(nm) (ε, $M^{-1}cm^{-1}$)): 332 (1.6 x $10^3$), 448 (3300), 505 (148), 596 (55), 670 (48). Evans' method ($C_6D_6$): 1.88 μB. IR ($C_6H_6$): 2038 $cm^{-1}$ (Co-$N_2$). Anal. Calcd for $C_{46}H_{80}N_7P_3CoZr$: C, 56.71; H, 8.28; N, 10.06. Found: C, 56.54; H, 8.23; N, 9.96.

**($\eta^2$-$NPhNH_2$)Zr($MesNP^iPr_2$)$_3$$CoN_2$ (4)**

A solution of phenylhydrazine (3.7 μL, 0.037 mmol) in $C_6H_6$ (1 mL) was layered onto a frozen solution of **1** (0.0375 g, 0.0375 mmol) in $C_6H_6$ (7 mL). The reaction mixture was warmed to room temperature and stirred for 30 min. The resulting yellow/orange solution was filtered through Celite, and the volatiles were removed from the filtrate in vacuo to yield a yellow/orange residue. The resulting residue was washed with cold (-35°C) *n*-pentane (4 mL) to yield product as a yellow-red powder (0.026 g, 0.025 mmol, 66.8%). Crystals suitable for X-ray diffraction were grown from a concentrated diethyl ether solution at -35°C. $^1$H NMR (400 MHz, $C_6D_6$): δ 7.69 (s, 6H, H-Ar), 7.34 (t, 1H, *p*-H(N-Ar)), 7.02 (m, 2H, *m*-H(N-Ar)), 6.58 (d, 2H, *o*-H(N-Ar)), 5.82 (bs, 18H, CH(C$H_3$)$_2$), 2.58 (s, 18H, CH(C$H_3$)$_2$), 2.13 (s, 9H, *p*-Me-Ar), -1.56 (bs, 18H, *o*-Me -Ar), (not observed; $NH_2$ and C*H*($CH_3$)$_2$). UV-vis ($C_6H_6$ , λ(nm) (ε, $M^{-1}cm^{-1}$)): 344 (2.5 x $10^3$), 456 (450), 513(340), 681 (50). Evans' method ($C_6D_6$): 2.02 μB. IR ($C_6H_6$): 2044 $cm^{-1}$ (Co-$N_2$). Despite repeated attempts, samples of **4** suitable for combustion analysis could not be obtained owing to small amounts of impurities, including decomposed byproducts of H-atom addition and small amounts of **5.**

**($\eta^2$-$NPhNH_2$)Zr($MesNP^iPr_2$)$_3$Co(NHPh) (5)**

A solution of phenylhydrazine (7.4 μL, 0.075 mmol) in $C_6H_6$ (1 mL) was layered onto a frozen solution of **1** (0.0375 g, 0.0375 mmol) in $C_6H_6$ (7 mL). The reaction mixture was warmed to room temperature and stirred for 30 min. The resulting red/purple solution was filtered through Celite, and the volatiles were removed from the filtrate in vacuo to yield a red/purple residue. The resulting residue was extracted into cold (-35°C) *n*-pentane (4 mL) and filtered through Celite. Volatiles were removed from the filtrate in vacuo to yield analytically pure product as a purple/red powder (0.030 g, 0.030 mmol, 72.8%). Crystals suitable for X-ray diffraction were grown from a concentrated pentane solution at -35°C. $^1$H NMR (400 MHz, $C_6D_6$): δ 13.65 (bs), 7.08 (s), 7.06 (s), 6.73(t), 6.46 (bs), 6.36 (d), 5.54 (bs), 5.25(bs), 2.10 (bs), 1.81 (s), -0.60 (bs). UV-vis ($C_6H_6$ , λ(nm) (ε, $M^{-1}cm^{-1}$)): 336 (2.3 x $10^3$), 430 (880), 578 (990), 515 (1.1 x $10^3$), 690 (280), 807 (140). Evans' method ($C_6D_6$): 2.78 μB. IR ($C_6H_6$): 3468, 3381, 3280 $cm^{-1}$ (N-H). Anal. Calcd for $C_{45}H_{78}N_7P_3CoZr$: C, 62.21; H, 8.06; N, 7.64. Found:C, 62.25; H, 8.17; N, 7.64.

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**Figure S1.** $^{1}H$ NMR spectrum of $(\eta^2\text{-}NHNH_2)Zr(MesNP^iPr_2)_3CoN_2$ **(2)** ($C_6D_6$, 400 MHz).

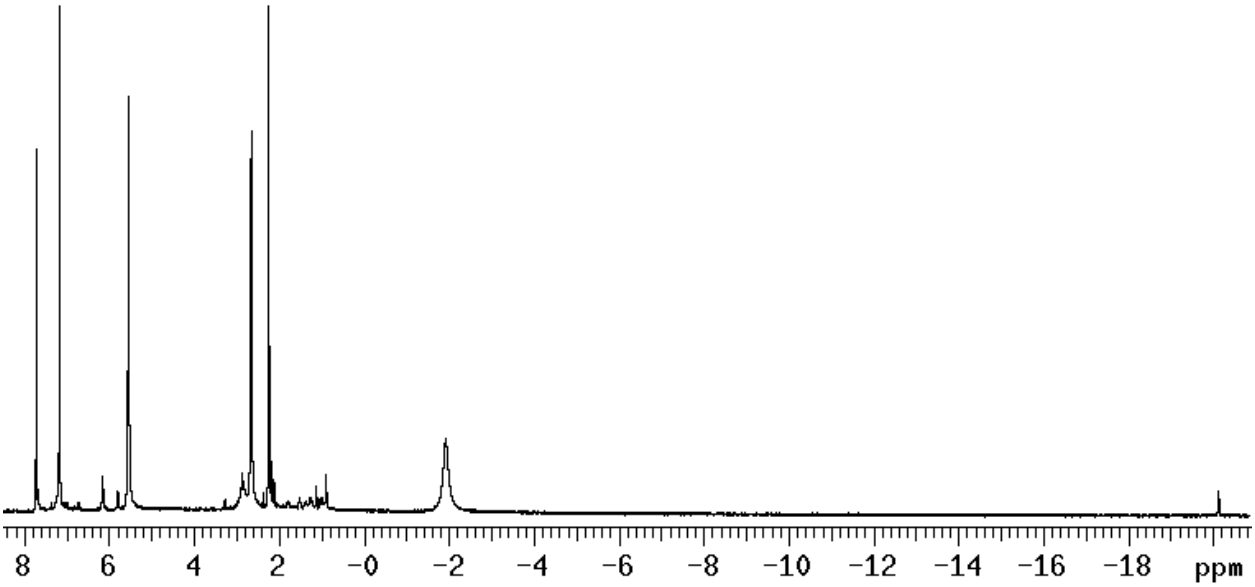


**Figure S2.** $^{1}H$ NMR spectrum of $(\eta^2\text{-}MeN_2H_3)Zr(MesNP^iPr_2)_3CoN_2$ **(3)** ($C_6D_6$, 400 MHz).

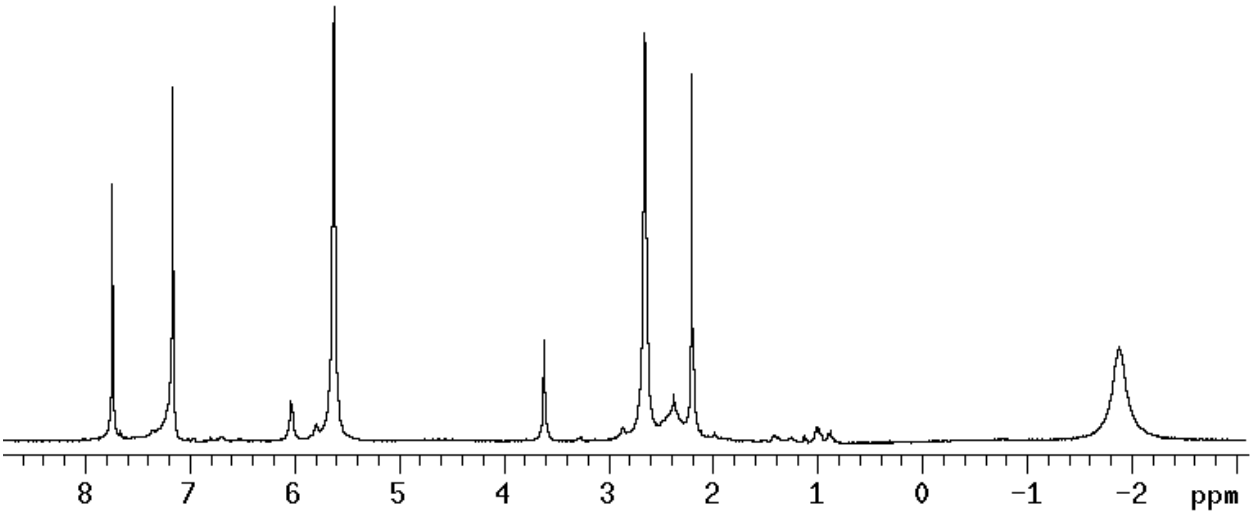

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**Figure S3.** $^{1}$H NMR spectrum of ($\eta^2$-NPhNH$_2$)Zr(MesNP$^{i}$Pr$_2$)$_3$CoN$_2$ **(4)** ($C_6D_6$, 400 MHz).

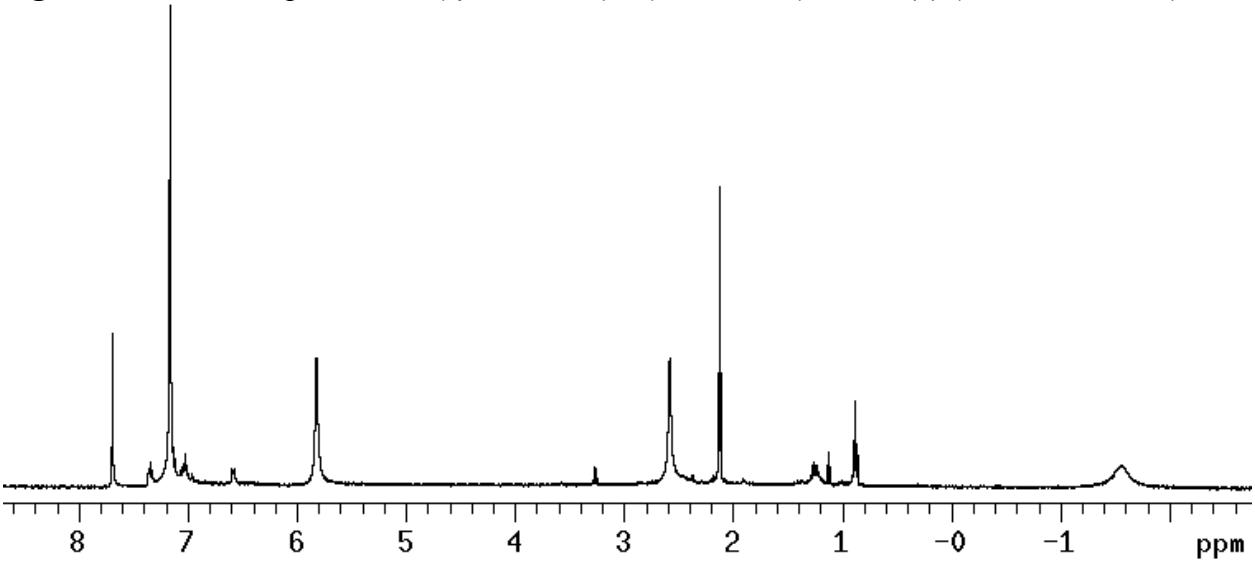



**Figure S4.** $^{1}$H NMR spectrum of ($\eta^2$-NPhNH$_2$)Zr(MesNP$^{i}$Pr$_2$)$_3$Co(NHPh**) (5)** ($C_6D_6$, 400 MHz).

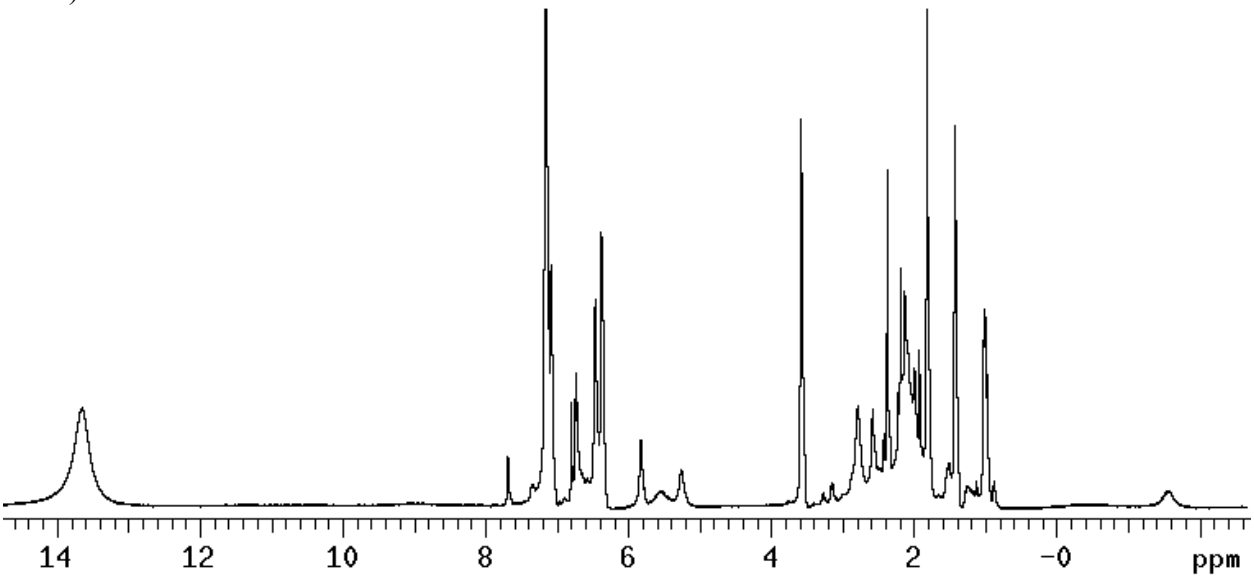


**Figure S5.** $^1$H NMR spectrum of volatiles resulting from formation of complex **2** ($C_6D_6$, 400 MHz).

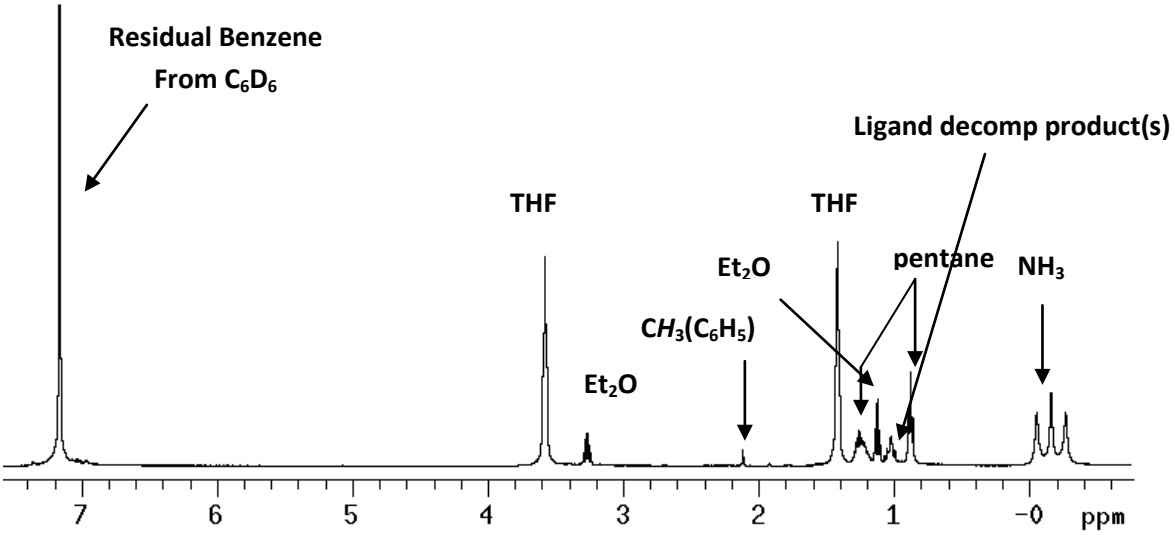
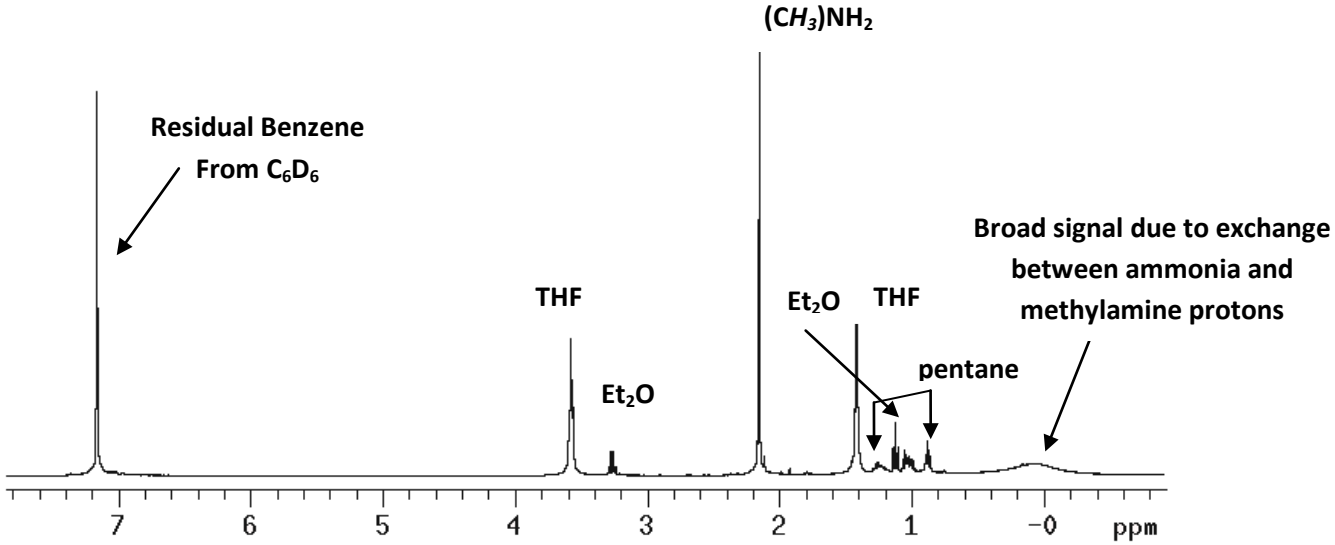



**Figure S6.** $^1$H NMR spectrum of volatiles resulting from formation of complex **3** ($C_6D_6$, 400 MHz).




**Note:** In the presence of exchangeable protons, $NH_3$ is often difficult to detect by $^1$H NMR and either appears as a broad singlet or a very broad hump. As shown in Figure S6, a mixture of $NH_3$ and $MeNH_2$ leads to a very sharp peak for the Me group of $MeNH_2$, but a broad lump around 0 corresponding to protons exchanging between the nitrogens of $MeNH_2$ and $NH_3$. $NH_3$ was unambiguously identified in Figure S5 via comparison with a literature spectrum.[8]

[8] Askevold, B.; Nieto, J. T.; Tussupbayev, S.; Diefenbach, M.; Herdtweck, E.; Hotlhausen, M. C.; Schneider, S. *Nature Chem.* **2011**, *3*, 532-537

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**Figure S7.** Cyclic voltammogram of ($\eta^2$-$NHNH_2$)Zr(MesNP$^i$Pr$_2$)$_3$CoN$_2$ **(2)** (2 mM in 0.4 M [$^n$Bu$_4$N][PF$_6$] in THF, scan rate = 100 mV/s, potentials are referenced to Fc, starting potential: 1.02 V, lowest potential: -3.25 V)

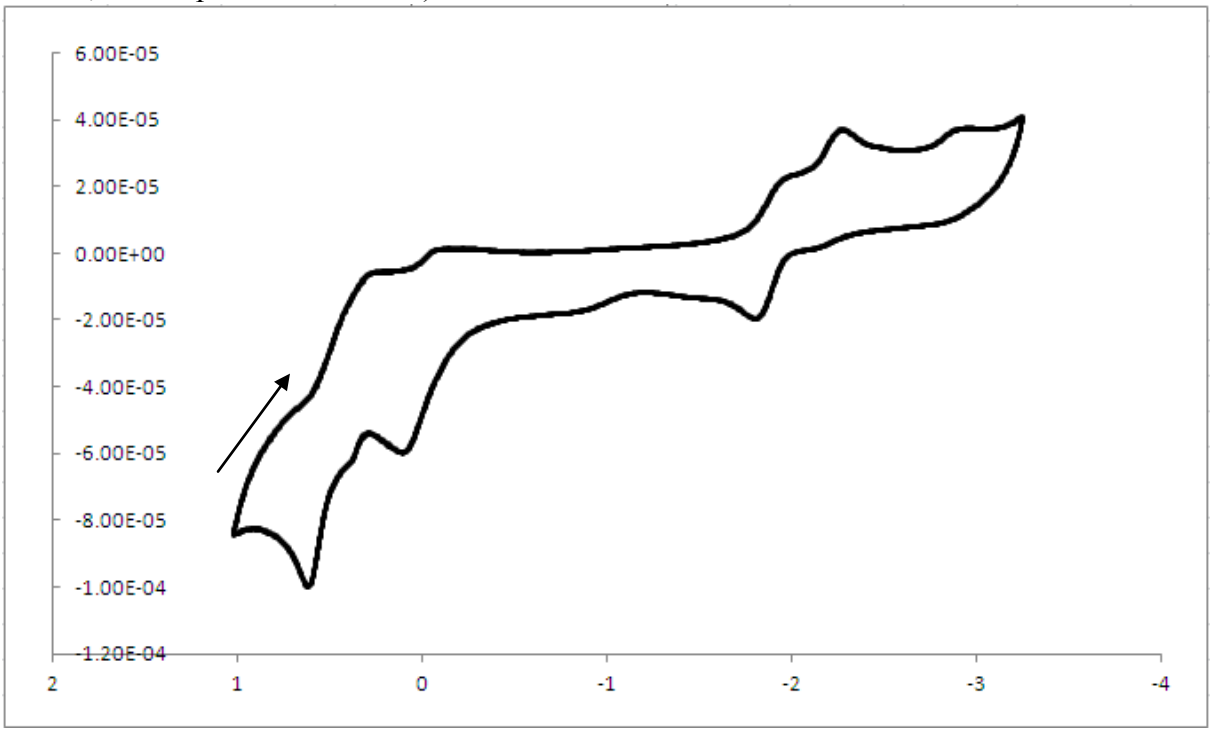

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**Figure S8.** Cyclic voltammogram of ($\eta^2$-$MeN_2H_3$)Zr($MesNP^iPr_2$)$_3$$CoN_2$ **(3)** (2 mM in 0.4 M [$^n$Bu$_4$N[$PF_6$] in THF, scan rate = 100 mV/s, potentials are referenced to Fc, starting potential: -0.46 V, lowest potential: -2.80 V, highest potential: 1.34 V)

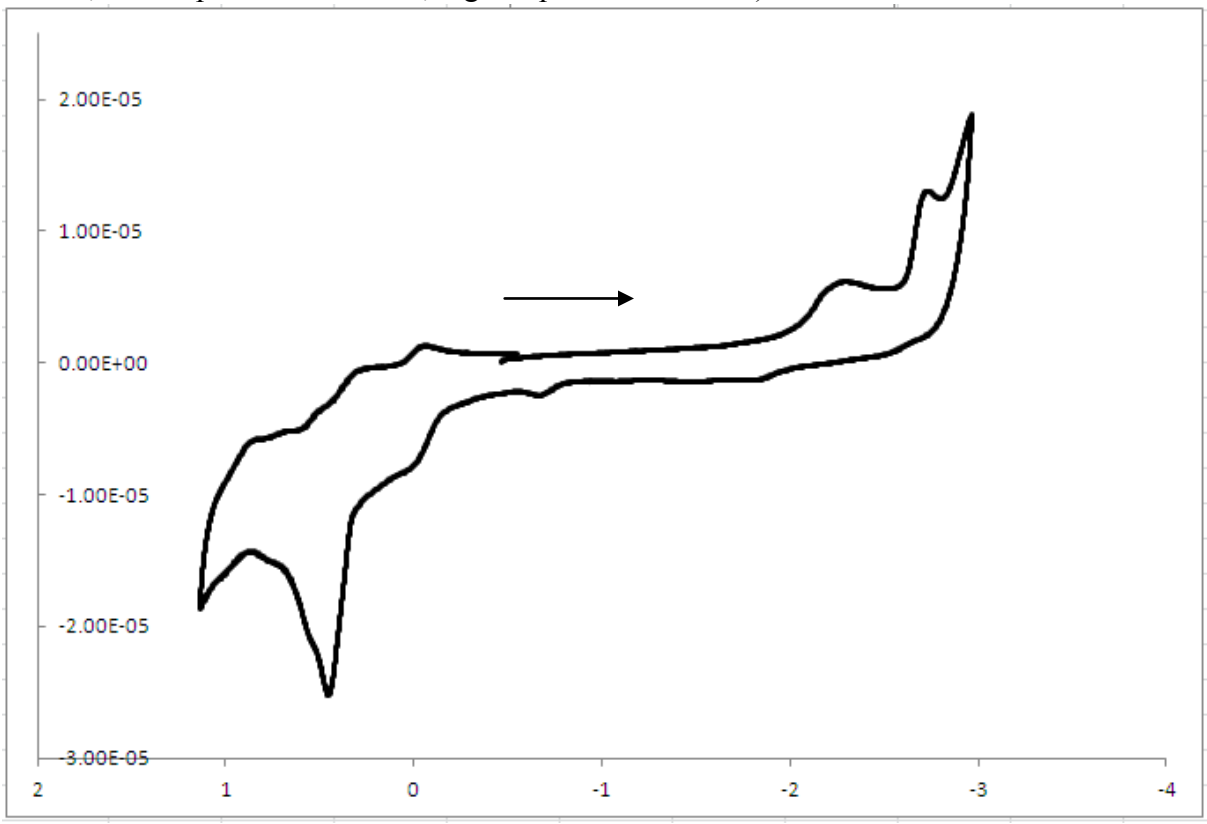

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**Figure S9.** Cyclic voltammogram of ($\eta^2$-$NPhNH_2$)Zr($MesNP^iPr_2$)$_3$$CoN_2$ **(4)** (2 mM in 0.4 M [$^n$Bu$_4$N][$PF_6$] in THF, scan rate = 100 mV/s, potentials are referenced to Fc, starting potential: 0.97 V, lowest potential: -2.99 V)

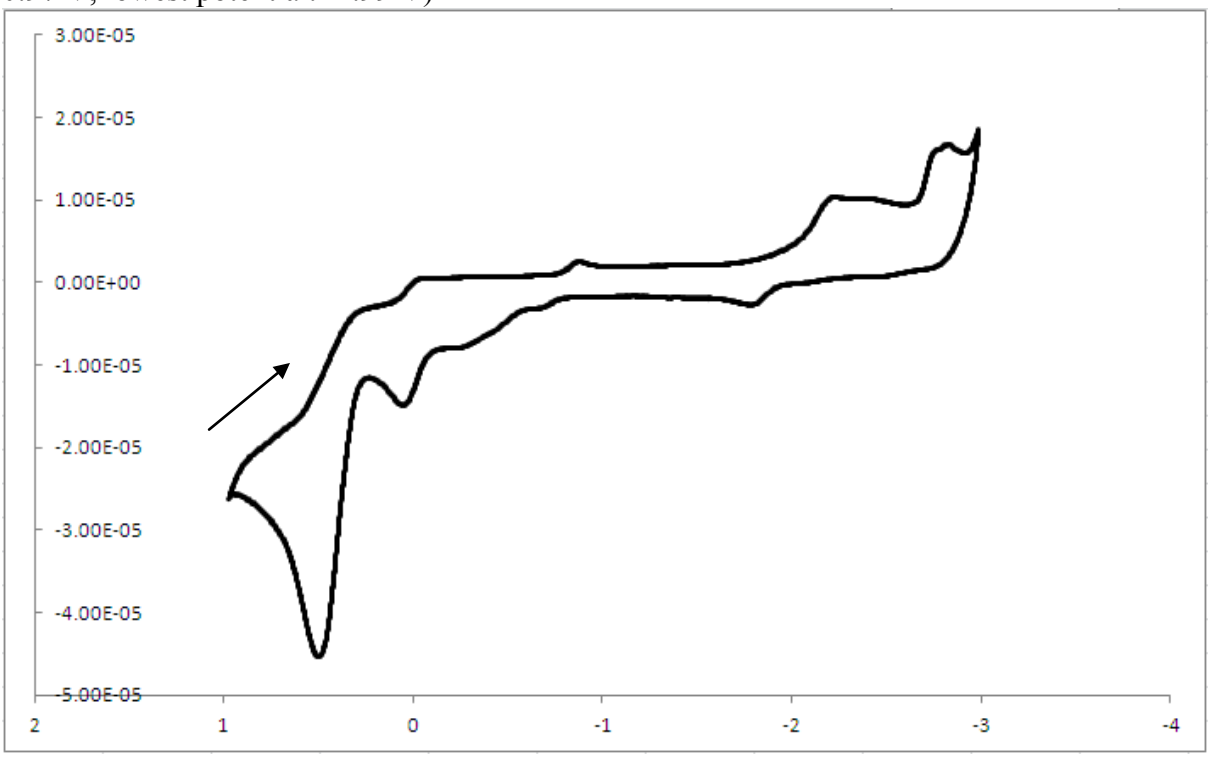

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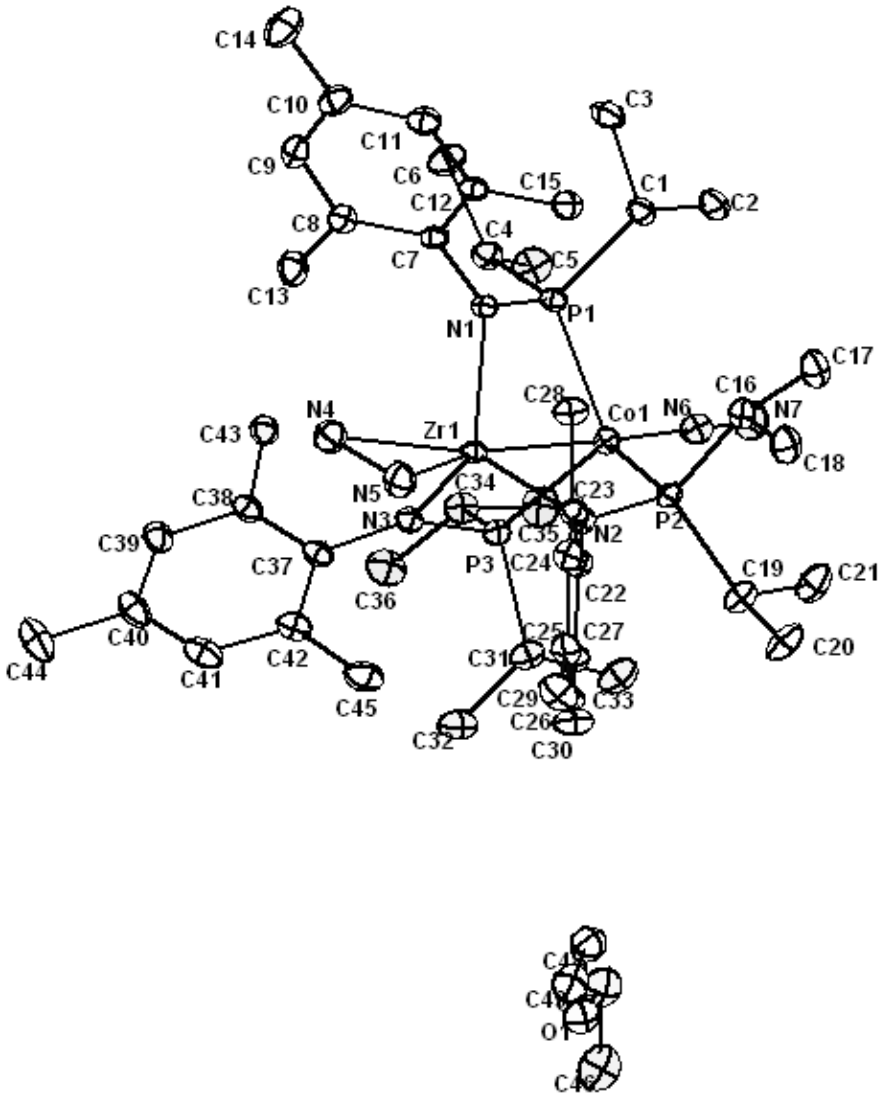
**Table S1. X-ray Diffraction Experimental Details for 2, 4, and 5.**

| | **2** | **4** | **5** |
|---|---|---|---|
| chemical formula | $C_{49}H_{88}CoN_7O_1P_3Zr$ | $C_{57}H_{97}CoN_7O_{1.5}P_3Zr$ | $C_{59}H_{93}CoN_6O_{0.5}P_3Zr$ |
| CCDC # | 892503 | 892502 | 892504 |
| fw | 1034.36 | 1147.53 | 1137.50 |
| $T$ (K) | 120 K | 120 K | 120 K |
| $\lambda$ (Å) | 0.71073 Å | 0.71073 | 0.71073 |
| $a$ (Å) | 12.1683(4) | 13.6949(8) | 12.4014(10) |
| $b$ (Å) | 12.8589(4) | 20.9745(12) | 12.4582(10) |
| $c$ (Å) | 17.2789(5) | 21.5785(12) | 21.3579(16) |
| $\alpha$ (deg) | 97.3550(10) | 97.813(3) | 94.279(4) |
| $\beta$ (deg) | 96.2060(10) | 91.989(3) | 98.424(4) |
| $\gamma$ (deg) | 94.278(2) | 104.989(3) | 114.230(5) |
| $V$ (Å$^3$) | 2654.94(14) | 5917.9(6) | 2943.2(4) |
| space group | *P*-1 | *P*-1 | *P*-1 |
| $Z$ | 2 | 4 | 4 |
| $D_{calcd}$ (g/cm$^3$) | 1.294 | 1.288 | 1.283 |
| $\mu$ (cm$^{-1}$) | 6.40 | 5.82 | 5.83 |
| $R1$ ($I > 2\sigma$) | 0.0265 | 0.0477 | 0.0441 |
| $wR2$ (all data) | 0.0655 | 0.1240 | 0.0896 |

**Figure S10.** Fully labeled ellipsoid representation of $(\eta^2\text{-}NHNH_2)Zr(MesNP^iPr_2)_3CoN_2$ **(2)**



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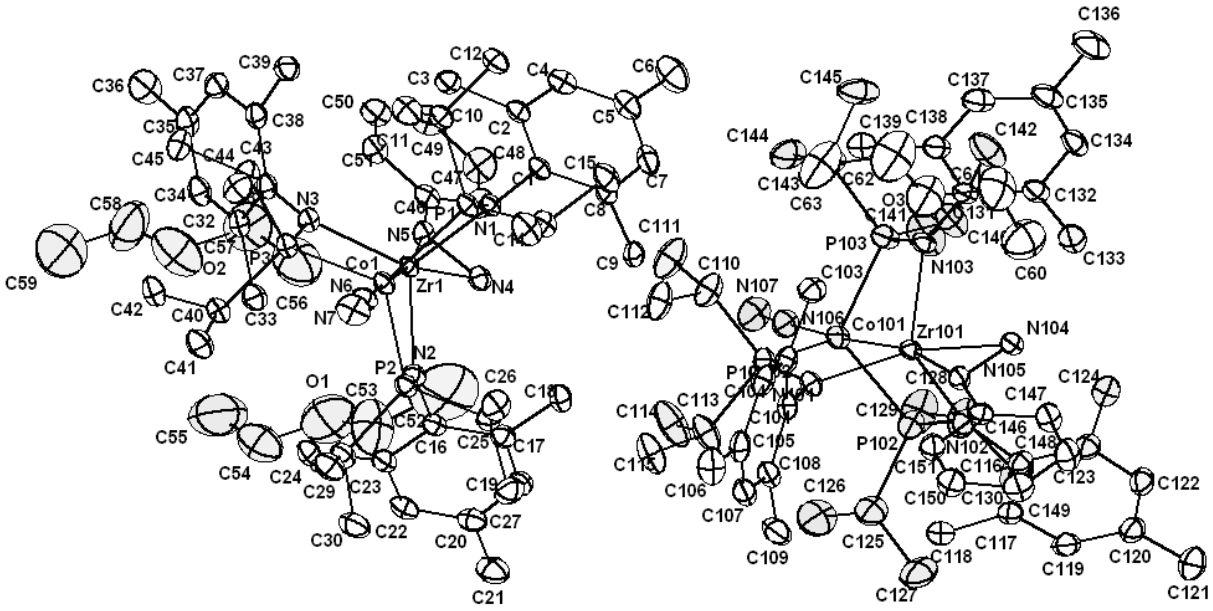
**X-Ray data collection, solution, and refinement for 2.** Data collection was carried out at 120K, using a frame time of 10 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of eight phi and five omega scan sets, with 0.5° steps in phi or omega; completeness was 99.2%. A total of 4745 frames were collected. Final cell constants were obtained from the xyz centroids of 9794 reflections after integration. From the systematic absences, the observed metric constants and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SIR-92*,[9] and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.[10] All non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93--0.98 Å and $U_{iso}$ (H) in the range 1.2-1.5 times $U_{eq}$ of the parent atom), after which the positions were refined with riding constraints.[11] The H atoms bonded to the hydrazine were readily located on a ΔF map calculated using only low angle data. The final least-squares refinement converged to $R_1 = 0.0265$ ($I > 2\sigma(I)$, 12688 data) and $wR_2 = 0.0655$ ($F^2$, 15426 data, 559 parameters). The final CIF is available as supporting material.

[9] Altomare, A; Cascarano, G; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst*. **1994**, *27*, 435. Palatinus, L., Chapuis, G.; *J. Appl. Cryst*. **2007**, 40, 786.

[10] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Cryst.* **2003**, *36*, 1487; Prout, C.K;. Pearce, L.J. CAMERON, Chemical Crystallography Laboratory, Oxford, UK, 1996.

[11] Cooper, R. I.; Thompson, A. L.; Watkin, D. J. *J. Appl. Cryst.* **2010**, *43*, 1100–1107.

**Figure S11.** Fully labeled ellipsoid representation of ($\eta^2$-$PhN_2H_3$)Zr(MesNP$^i$Pr$_2$)$_3$CoN$_2$ (**4**)



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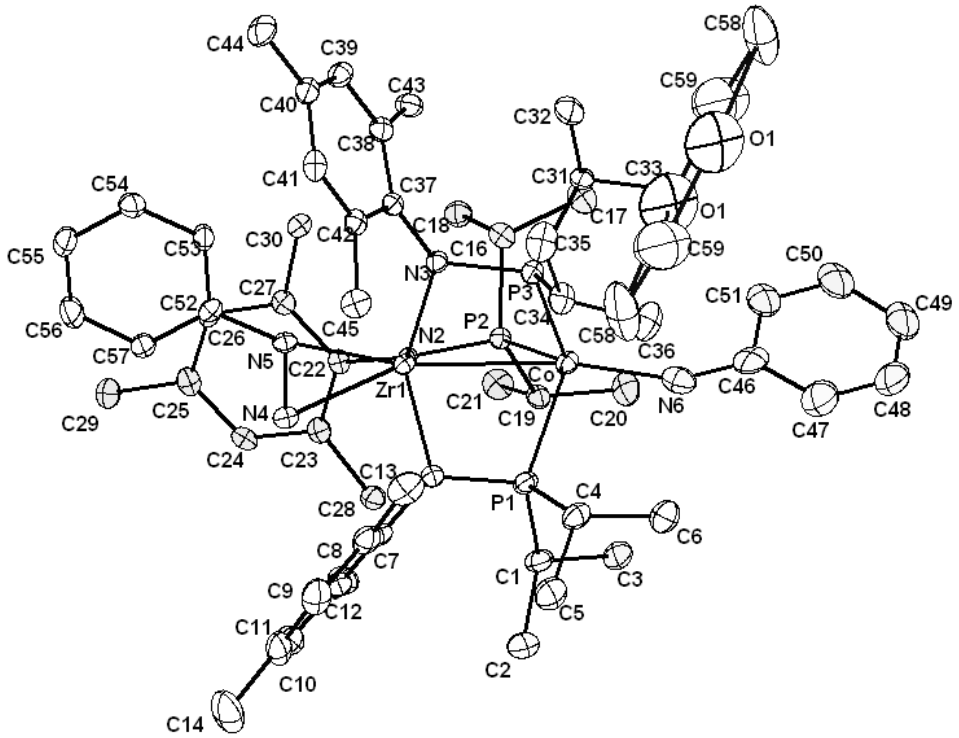
**X-Ray data collection, solution, and refinement for 4.** Data collection was carried out at 120K, using a frame time of 20 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of four phi and two omega scan sets, with 0.5° steps in phi or omega; completeness was 99.3%. A total of 3175 frames were collected. Final cell constants were obtained from the xyz centroids of 9806 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The asymmetric unit contains two molecules of the complex. The second molecule is numbered similarly to the first, with atom sequence numbers exactly 100 greater than those of the reference molecule. The structure was solved using *SuperFlip*,[12] and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program. All non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93--0.98 Å and $U_{iso}$ (H) in the range 1.2-1.5 times $U_{eq}$ of the parent atom), after which the positions were refined with riding constraints. The final least-squares refinement converged to $R_1 = 0.0477$ ($I > 2\sigma(I)$, 23306 data) and $wR_2 = 0.1240$ ($F^2$, 31756 data, 1270 parameters). The final CIF is available as supporting material.

[12] Palatinus, L.; Chapuis, G.; *J. Appl. Cryst*. **2007**, 40, 786.

**Figure S12.** Fully labeled ellipsoid representation of ($\eta^2$-$NPhNH_2$)Zr($MesNP^iPr_2$)$_3$Co(NHPh) **(5)**



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**X-Ray data collection, solution, and refinement for 5.** Data collection was carried out at 120K, using a frame time of 40 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of three phi and five omega scan sets, with 0.5° steps in phi or omega; completeness was 99.6%. A total of 2486 frames were collected. Final cell constants were obtained from the xyz centroids of 5383 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SIR-92*, and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program. All non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93--0.98 Å and $U_{iso}$ (H) in the range 1.2-1.5 times $U_{eq}$ of the parent atom), after which the positions were refined with riding constraints. The asymnetric unit contains one-half molecule of ether solvate, disordered about a center of symmetry at (0, 0, ½). The midpoint of one of the O-C bonds lies on the center of symmetry. The disorder was modeled by assigning fixed occupancies (required by symmetry) of 0.5 to methyl atom C(59), and 1.0 to atom C(58) [both a $-CH_2$ or $-CH_3$ moiety]. Methylene atom C(60) was assigned the same coordinates as atom O(1) and was refined using an EQUIVALENCE constraint; [10] each had a fixed occupancy, as above, required by symmetry, of 0.5. The final least-squares refinement converged to $R_1 = 0.0441$ ($I > 2\sigma(I)$, 7845 data) and $wR_2 = 0.0896$ ($F^2$, 10798 data, 633 parameters). The final CIF is available as supporting material.

**Figure S13.** Plot of Mulliken spin density surface derived from DFT calculations (BP86/LANL2TZ(f)/6-311+G(d)/D95V).

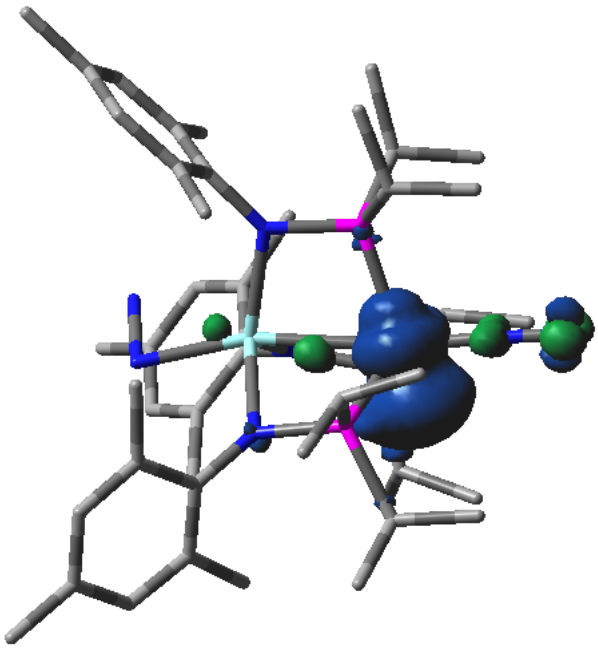
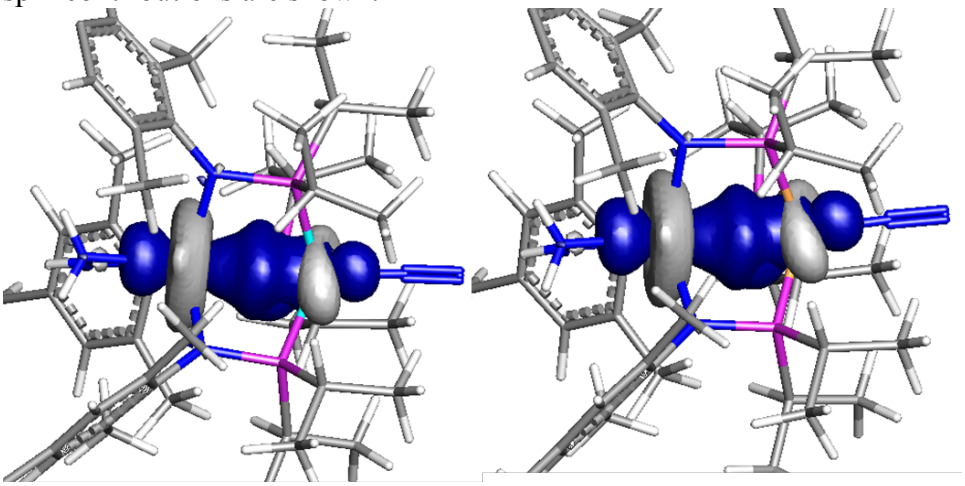


**Figure S14.** Donor-acceptor interactions in complex **2** between the filled $d_{z2}$ orbital on Co and the empty $d_{z2}$ orbital on Zr. Both alpha ($E_{del}$ = 41.3 kcal/mol) and beta ($E_{del}$ = 68.4 kcal/mol) spin contributions are shown.



Alpha spin
$E_{del}$ = 41.3 kcal/mol

Beta spin
$E_{del}$ = 68.4 kcal/mol

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**Figure S15.** Calculated LUMO and SOMO (isodensity 0.04) of complex **2** (BP86/LANL2TZ(f)/6-311G(d)/D95V).

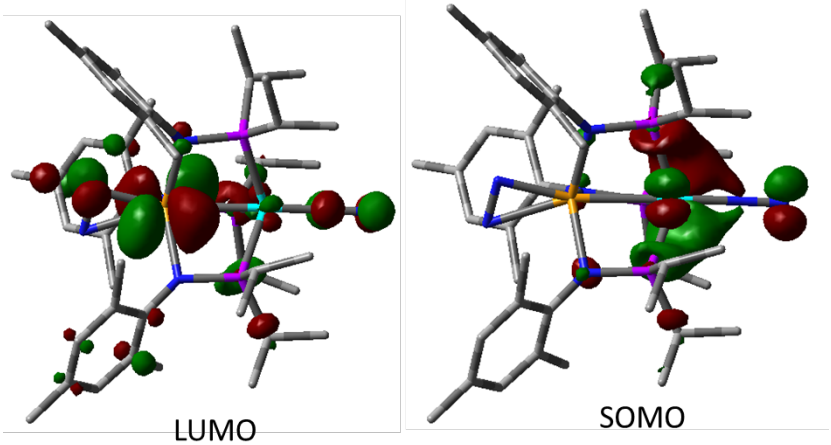

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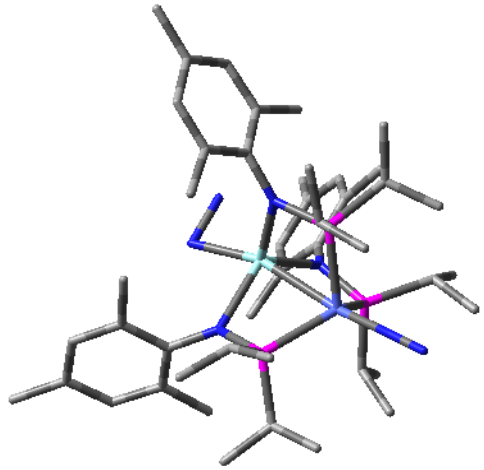
**Table S2.** X, Y, Z coordinates of the optimized structure of **2**.



| Tag | Symbol | X | Y | Z |
|---|---|---|---|---|
| 1 | Co | 0.1549 | 0.011371 | -2.10161 |
| 2 | Zr | -0.01837 | -0.03798 | 0.648073 |
| 3 | P | -0.8278 | 2.002413 | -1.40285 |
| 4 | P | 2.311192 | -0.04637 | -1.29238 |
| 5 | P | -1.2365 | -1.73289 | -1.52553 |
| 6 | N | -0.69069 | 2.005461 | 0.317947 |
| 7 | N | 2.141216 | -0.42121 | 0.370744 |
| 8 | N | -1.49334 | -1.59841 | 0.171038 |
| 9 | N | 0.142346 | 0.231899 | -3.90434 |
| 10 | N | 0.137772 | 0.317841 | -5.04129 |
| 11 | N | 0.427548 | -0.27452 | 2.653452 |
| 12 | N | -0.95993 | -0.00092 | 2.822806 |
| 13 | C | -0.01918 | 3.595751 | -2.08621 |
| 14 | C | 0.016482 | 3.63354 | -3.6388 |
| 15 | C | -0.55762 | 4.963993 | -1.57273 |
| 16 | C | -2.68677 | 2.134861 | -1.81358 |
| 17 | C | -3.00668 | 1.762079 | -3.28583 |
| 18 | C | -3.42502 | 3.447698 | -1.43244 |
| 19 | C | -1.01673 | 3.006843 | 1.30737 |
| 20 | C | -2.27035 | 2.97359 | 2.01832 |
| 21 | C | -2.53255 | 3.92219 | 3.040624 |
| 22 | C | -1.60142 | 4.92178 | 3.408946 |
| 23 | C | -0.36024 | 4.924596 | 2.731313 |
| 24 | C | -0.04932 | 3.996613 | 1.705072 |
| 25 | C | -3.34 | 1.938582 | 1.719628 |

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| | | | | |
|---|---|---|---|---|
| 26 | C | -1.92374 | 5.95238 | 4.481304 |
| 27 | C | 1.321476 | 4.096766 | 1.05858 |
| 28 | C | 3.374867 | 1.530469 | -1.44253 |
| 29 | C | 3.368429 | 2.119411 | -2.87918 |
| 30 | C | 4.827336 | 1.487441 | -0.88976 |
| 31 | C | 3.300221 | -1.43126 | -2.1716 |
| 32 | C | 4.751847 | -1.69761 | -1.67802 |
| 33 | C | 3.312976 | -1.2777 | -3.71778 |
| 34 | C | 3.121354 | -0.80766 | 1.359112 |
| 35 | C | 3.654256 | 0.152192 | 2.292445 |
| 36 | C | 4.580851 | -0.25884 | 3.282453 |
| 37 | C | 5.004703 | -1.60388 | 3.418037 |
| 38 | C | 4.430265 | -2.54847 | 2.539099 |
| 39 | C | 3.500834 | -2.18383 | 1.529176 |
| 40 | C | 3.221659 | 1.605571 | 2.275747 |
| 41 | C | 6.032409 | -2.00876 | 4.465187 |
| 42 | C | 2.924517 | -3.29959 | 0.673699 |
| 43 | C | -0.31196 | -3.37718 | -1.82437 |
| 44 | C | -1.04311 | -4.69323 | -1.44114 |
| 45 | C | 0.289699 | -3.49302 | -3.25115 |
| 46 | C | -2.90581 | -1.90782 | -2.44629 |
| 47 | C | -2.71434 | -1.89666 | -3.9893 |
| 48 | C | -3.83647 | -3.09451 | -2.06143 |
| 49 | C | -2.32952 | -2.34386 | 1.081032 |
| 50 | C | -3.7272 | -2.04319 | 1.246009 |
| 51 | C | -4.49597 | -2.74599 | 2.212017 |
| 52 | C | -3.94293 | -3.74078 | 3.048643 |
| 53 | C | -2.55702 | -4.00056 | 2.910068 |
| 54 | C | -1.74664 | -3.32787 | 1.961592 |
| 55 | C | -4.44689 | -0.98067 | 0.429661 |
| 56 | C | -4.79589 | -4.50702 | 4.049304 |
| 57 | C | -0.26543 | -3.65947 | 1.920657 |
| 58 | H | 1.023237 | 3.476786 | -1.72859 |
| 59 | H | 0.404045 | 2.706086 | -4.0853 |
| 60 | H | 0.667255 | 4.46883 | -3.96694 |
| 61 | H | -0.98913 | 3.819968 | -4.05791 |
| 62 | H | -1.44863 | 5.274319 | -2.1454 |
| 63 | H | -0.82365 | 4.963088 | -0.50473 |
| 64 | H | 0.216816 | 5.741208 | -1.73458 |
| 65 | H | -3.07772 | 1.320453 | -1.16847 |
| 66 | H | -4.09717 | 1.596268 | -3.40177 |
| 67 | H | -2.72279 | 2.572904 | -3.98072 |
| 68 | H | -2.48121 | 0.847269 | -3.60004 |

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| | | | | |
|---|---|---|---|---|
| 69 | H | -4.51712 | 3.257915 | -1.3889 |
| 70 | H | -3.10864 | 3.858277 | -0.45954 |
| 71 | H | -3.26552 | 4.225511 | -2.20041 |
| 72 | H | 0.955292 | -0.48819 | 3.509771 |
| 73 | H | -1.17283 | 0.873312 | 3.324801 |
| 74 | H | -1.52422 | -0.7864 | 3.17922 |
| 75 | H | -3.49891 | 3.871183 | 3.562121 |
| 76 | H | 0.400813 | 5.668599 | 3.007223 |
| 77 | H | -2.88964 | 0.980011 | 1.424733 |
| 78 | H | -3.98068 | 1.770681 | 2.605556 |
| 79 | H | -4.00228 | 2.258887 | 0.893822 |
| 80 | H | -2.67063 | 5.569092 | 5.200192 |
| 81 | H | -2.3416 | 6.877076 | 4.034903 |
| 82 | H | -1.02055 | 6.243101 | 5.048775 |
| 83 | H | 1.550631 | 3.181148 | 0.494272 |
| 84 | H | 2.10508 | 4.247832 | 1.822598 |
| 85 | H | 1.375493 | 4.953259 | 0.359653 |
| 86 | H | 2.786025 | 2.216508 | -0.79818 |
| 87 | H | 2.368457 | 2.070246 | -3.3407 |
| 88 | H | 3.689407 | 3.180354 | -2.85479 |
| 89 | H | 4.07426 | 1.580123 | -3.53654 |
| 90 | H | 5.178024 | 2.520072 | -0.68737 |
| 91 | H | 4.919843 | 0.906882 | 0.042644 |
| 92 | H | 5.519059 | 1.051898 | -1.63229 |
| 93 | H | 2.685886 | -2.32113 | -1.92793 |
| 94 | H | 5.457147 | -0.9779 | -2.12931 |
| 95 | H | 5.069423 | -2.70908 | -2.00443 |
| 96 | H | 4.860153 | -1.64103 | -0.58346 |
| 97 | H | 3.661707 | -2.22361 | -4.17883 |
| 98 | H | 4.011066 | -0.48252 | -4.03557 |
| 99 | H | 2.321617 | -1.03995 | -4.13466 |
| 100 | H | 4.976826 | 0.499558 | 3.972591 |
| 101 | H | 4.702792 | -3.60923 | 2.637032 |
| 102 | H | 3.69109 | 2.161888 | 3.107839 |
| 103 | H | 3.495662 | 2.109696 | 1.333928 |
| 104 | H | 2.12507 | 1.683845 | 2.379531 |
| 105 | H | 5.9031 | -1.43729 | 5.403246 |
| 106 | H | 7.064793 | -1.82 | 4.107939 |
| 107 | H | 5.959978 | -3.08451 | 4.70805 |
| 108 | H | 2.020572 | -2.95438 | 0.15006 |
| 109 | H | 2.660976 | -4.17247 | 1.298838 |
| 110 | H | 3.648764 | -3.64886 | -0.08716 |
| 111 | H | 0.534364 | -3.24284 | -1.1195 |

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| | | | | |
|---|---|---|---|---|
| 112 | H | -0.29816 | -5.50182 | -1.29512 |
| 113 | H | -1.63489 | -4.60386 | -0.51482 |
| 114 | H | -1.72041 | -5.02059 | -2.24974 |
| 115 | H | 1.048416 | -4.30133 | -3.2739 |
| 116 | H | 0.775456 | -2.55737 | -3.57505 |
| 117 | H | -0.48355 | -3.7478 | -3.99748 |
| 118 | H | -3.41243 | -0.96254 | -2.16744 |
| 119 | H | -1.98235 | -1.14596 | -4.32679 |
| 120 | H | -3.68325 | -1.67562 | -4.4798 |
| 121 | H | -2.38175 | -2.88473 | -4.35578 |
| 122 | H | -3.86113 | -3.30181 | -0.9803 |
| 123 | H | -3.52465 | -4.01942 | -2.57715 |
| 124 | H | -4.87073 | -2.8721 | -2.39461 |
| 125 | H | -5.56246 | -2.49619 | 2.30806 |
| 126 | H | -2.0849 | -4.75022 | 3.560462 |
| 127 | H | -5.12572 | -1.43582 | -0.31636 |
| 128 | H | -3.73097 | -0.34215 | -0.1079 |
| 129 | H | -5.0661 | -0.33987 | 1.083821 |
| 130 | H | -5.71702 | -3.95224 | 4.304203 |
| 131 | H | -5.10504 | -5.49035 | 3.641571 |
| 132 | H | -4.24398 | -4.70284 | 4.987427 |
| 133 | H | -0.02004 | -4.43262 | 2.671443 |
| 134 | H | 0.04078 | -4.0367 | 0.930776 |
| 135 | H | 0.35514 | -2.76844 | 2.130472 |

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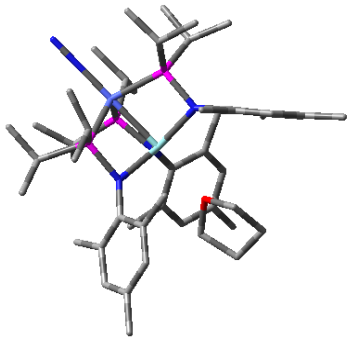
**Table S3.** X, Y, Z coordinates of the optimized structure of **1**.



| Tag | Symbol | X | Y | Z |
|---|---|---|---|---|
| 1 | Zr | -0.00491 | 0.080652 | 0.175459 |
| 2 | Co | -0.13708 | -1.09638 | -1.91933 |
| 3 | P | 1.413117 | -2.2208 | -0.71369 |
| 4 | P | 0.494825 | 1.005572 | -2.47509 |
| 5 | P | -2.2202 | -1.2136 | -1.03062 |
| 6 | O | 0.250961 | 1.424382 | 2.257018 |
| 7 | N | 1.710862 | -1.1857 | 0.660835 |
| 8 | N | 0.350851 | 1.882024 | -0.98114 |
| 9 | N | -2.06456 | -0.51961 | 0.565854 |
| 10 | N | -0.274 | -1.98899 | -3.49246 |
| 11 | N | -0.36902 | -2.54951 | -4.48339 |
| 12 | C | 2.696803 | -1.24388 | 1.704401 |
| 13 | C | 2.323532 | -1.66973 | 3.031025 |
| 14 | C | 3.282473 | -1.6914 | 4.072457 |
| 15 | C | 4.625739 | -1.28365 | 3.875155 |
| 16 | C | 4.967816 | -0.80443 | 2.590927 |
| 17 | C | 4.041937 | -0.76691 | 1.514036 |
| 18 | C | 0.896854 | -2.06827 | 3.351367 |
| 19 | C | 5.651005 | -1.36221 | 4.9969 |
| 20 | C | 4.53202 | -0.18788 | 0.196568 |
| 21 | C | 3.063125 | -2.61031 | -1.60663 |
| 22 | C | 4.164506 | -3.34452 | -0.78935 |
| 23 | C | 2.840219 | -3.37053 | -2.94373 |
| 24 | C | 0.824679 | -3.88438 | 0.021916 |
| 25 | C | 1.760966 | -4.63539 | 1.010262 |
| 26 | C | 0.29248 | -4.86439 | -1.05791 |
| 27 | C | 0.521316 | 3.263921 | -0.62703 |
| 28 | C | -0.56532 | 4.203833 | -0.72385 |
| 29 | C | -0.39 | 5.541189 | -0.27849 |

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| | | | | |
|---|---|---|---|---|
| 30 | C | 0.825216 | 6.007639 | 0.271464 |
| 31 | C | 1.881719 | 5.070635 | 0.386573 |
| 32 | C | 1.756716 | 3.727213 | -0.0452 |
| 33 | C | -1.92468 | 3.832871 | -1.29723 |
| 34 | C | 0.999844 | 7.455698 | 0.706535 |
| 35 | C | 2.952016 | 2.807557 | 0.123031 |
| 36 | C | -0.5534 | 1.879255 | -3.81673 |
| 37 | C | -0.25014 | 3.37381 | -4.12568 |
| 38 | C | -0.56752 | 1.079385 | -5.14888 |
| 39 | C | 2.310052 | 1.188573 | -3.03913 |
| 40 | C | 2.834367 | 2.609865 | -3.38114 |
| 41 | C | 2.676014 | 0.195617 | -4.17469 |
| 42 | C | -3.00961 | -0.43958 | 1.648998 |
| 43 | C | -3.10639 | -1.48653 | 2.634222 |
| 44 | C | -4.00194 | -1.35812 | 3.726098 |
| 45 | C | -4.82858 | -0.22401 | 3.903856 |
| 46 | C | -4.70742 | 0.814649 | 2.95103 |
| 47 | C | -3.82341 | 0.733873 | 1.84486 |
| 48 | C | -2.28356 | -2.75962 | 2.543828 |
| 49 | C | -5.8103 | -0.1306 | 5.06314 |
| 50 | C | -3.74148 | 1.925822 | 0.908714 |
| 51 | C | -2.94389 | -2.97814 | -0.86848 |
| 52 | C | -3.03128 | -3.68863 | -2.24852 |
| 53 | C | -4.29773 | -3.17018 | -0.12329 |
| 54 | C | -3.54794 | -0.18237 | -1.93627 |
| 55 | C | -3.52408 | -0.39749 | -3.47325 |
| 56 | C | -5.01107 | -0.2638 | -1.42051 |
| 57 | C | 1.453721 | 1.767709 | 3.064436 |
| 58 | C | 0.877357 | 2.033175 | 4.46047 |
| 59 | C | -0.41534 | 2.840973 | 4.137395 |
| 60 | C | -0.83981 | 2.33921 | 2.727864 |
| 61 | H | 2.966685 | -2.03515 | 5.067582 |
| 62 | H | 5.989391 | -0.44068 | 2.409211 |
| 63 | H | 0.794814 | -2.33538 | 4.419184 |
| 64 | H | 0.186065 | -1.24817 | 3.136647 |
| 65 | H | 0.571384 | -2.9324 | 2.7497 |
| 66 | H | 5.202949 | -1.11181 | 5.976577 |
| 67 | H | 6.496707 | -0.67272 | 4.821385 |
| 68 | H | 6.071768 | -2.3842 | 5.08281 |
| 69 | H | 5.217181 | -0.88364 | -0.32328 |
| 70 | H | 3.688497 | 0.02403 | -0.47687 |
| 71 | H | 5.090233 | 0.750886 | 0.369548 |
| 72 | H | 3.426147 | -1.59607 | -1.86305 |

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|---|---|---|---|---|
| 73 | H | 3.976758 | -4.43286 | -0.7735 |
| 74 | H | 4.243805 | -2.9974 | 0.252825 |
| 75 | H | 5.147893 | -3.19489 | -1.2805 |
| 76 | H | 3.784601 | -3.36771 | -3.52493 |
| 77 | H | 2.054333 | -2.9195 | -3.56734 |
| 78 | H | 2.568426 | -4.42654 | -2.76749 |
| 79 | H | -0.05158 | -3.5165 | 0.596278 |
| 80 | H | 1.158399 | -5.3168 | 1.645658 |
| 81 | H | 2.490735 | -5.26347 | 0.469346 |
| 82 | H | 2.322017 | -3.95777 | 1.673846 |
| 83 | H | -0.34398 | -5.63948 | -0.58437 |
| 84 | H | -0.30591 | -4.34649 | -1.82509 |
| 85 | H | 1.121497 | -5.39017 | -1.56545 |
| 86 | H | -1.23849 | 6.234592 | -0.37034 |
| 87 | H | 2.838496 | 5.392969 | 0.822196 |
| 88 | H | -2.74008 | 4.170889 | -0.63172 |
| 89 | H | -2.08808 | 4.315853 | -2.27933 |
| 90 | H | -2.01298 | 2.745447 | -1.43976 |
| 91 | H | 1.511693 | 8.050263 | -0.0766 |
| 92 | H | 1.611284 | 7.533712 | 1.624971 |
| 93 | H | 0.025851 | 7.939708 | 0.902413 |
| 94 | H | 3.642854 | 3.194918 | 0.894606 |
| 95 | H | 3.528486 | 2.714805 | -0.81576 |
| 96 | H | 2.646724 | 1.788096 | 0.405823 |
| 97 | H | -1.56666 | 1.810046 | -3.37334 |
| 98 | H | -0.00061 | 3.965125 | -3.23091 |
| 99 | H | 0.589862 | 3.465073 | -4.83621 |
| 100 | H | -1.13483 | 3.835178 | -4.61028 |
| 101 | H | -0.69076 | -0.00376 | -4.9961 |
| 102 | H | -1.40259 | 1.434434 | -5.78567 |
| 103 | H | 0.366607 | 1.238338 | -5.71791 |
| 104 | H | 2.821953 | 0.842011 | -2.11766 |
| 105 | H | 3.942552 | 2.621214 | -3.32597 |
| 106 | H | 2.563454 | 2.89493 | -4.41358 |
| 107 | H | 2.448209 | 3.387694 | -2.70157 |
| 108 | H | 2.30797 | 0.548919 | -5.15476 |
| 109 | H | 3.777964 | 0.09794 | -4.25241 |
| 110 | H | 2.248674 | -0.80309 | -3.99073 |
| 111 | H | -4.05107 | -2.17825 | 4.456953 |
| 112 | H | -5.31417 | 1.724126 | 3.067335 |
| 113 | H | -1.82831 | -3.00621 | 3.520188 |
| 114 | H | -2.91099 | -3.62216 | 2.24779 |
| 115 | H | -1.48482 | -2.65016 | 1.796036 |

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|---|---|---|---|---|
| 116 | H | -6.0066 | 0.92021 | 5.344623 |
| 117 | H | -5.43274 | -0.65971 | 5.957513 |
| 118 | H | -6.78546 | -0.5875 | 4.799999 |
| 119 | H | -2.77809 | 1.936207 | 0.379531 |
| 120 | H | -4.53708 | 1.902323 | 0.140513 |
| 121 | H | -3.85361 | 2.874446 | 1.466966 |
| 122 | H | -2.14728 | -3.47873 | -0.28297 |
| 123 | H | -2.11399 | -3.58211 | -2.8473 |
| 124 | H | -3.21735 | -4.77037 | -2.09222 |
| 125 | H | -3.87517 | -3.29589 | -2.84514 |
| 126 | H | -4.38216 | -4.22561 | 0.207926 |
| 127 | H | -4.41293 | -2.52452 | 0.760516 |
| 128 | H | -5.14934 | -2.97657 | -0.79843 |
| 129 | H | -3.16136 | 0.838203 | -1.73289 |
| 130 | H | -2.4973 | -0.39854 | -3.86999 |
| 131 | H | -3.99617 | -1.35647 | -3.75328 |
| 132 | H | -4.0954 | 0.410437 | -3.97448 |
| 133 | H | -5.08369 | -0.2913 | -0.32095 |
| 134 | H | -5.58193 | 0.615485 | -1.78397 |
| 135 | H | -5.51868 | -1.16065 | -1.81915 |
| 136 | H | 1.913315 | 2.678009 | 2.634475 |
| 137 | H | 2.144551 | 0.916264 | 2.99517 |
| 138 | H | 0.635894 | 1.077789 | 4.959577 |
| 139 | H | 1.577303 | 2.596935 | 5.101902 |
| 140 | H | -0.19601 | 3.92338 | 4.11258 |
| 141 | H | -1.20727 | 2.669166 | 4.886052 |
| 142 | H | -0.93107 | 3.159518 | 1.993254 |
| 143 | H | -1.75821 | 1.734654 | 2.744892 |