Supporting Information

Oxidative Addition Across Zr/Co Multiple Bonds in Early/Late Heterobimetallic Complexes

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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, *n*-pentane, tetrahydrofuran, diethyl ether, and dichloromethane were degassed and dried by sparging with ultra high purity argon gas followed by passage through a series of drying columns using a Seca Solvent System by Glass Contour[1]. All solvents were stored over 3-Å molecular sieves. Deuterated benzene and toluene were purchased from Cambridge Isotope Laboratories, Inc., degassed via repeated freeze-pump-thaw cycles, and dried over 3-Å molecular sieves. THF-d_8 was dried over Na/K alloy, vacuum-transferred, and degassed via repeated freeze-pump-thaw cycles. 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$_2$ (**2**),[2] (THF)Zr(MesNP^{i}Pr$_2$)$_3$Co,[2] and ClZr(^{i}PrNPPh$_2$)$_3$CoI[3] were synthesized using literature procedures. 2-iodopropane, iodomethane, and cyclohexyl chloride were sparged with N_2 and stored over 3-Å molecular sieves prior to use. All other chemicals were purchased from Aldrich, Strem or Alfa Aesar and used without further purification. NMR spectra were recorded at ambient temperature unless otherwise stated on Varian Inova 400 MHz instrument. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent and are reported in ppm. ^{31}P NMR chemical shifts

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

[2] Greenwood, B. P.; Rowe, G. T.; Chen, C.-H.; Foxman, B. M.; Thomas, C. M. *J. Am. Chem. Soc.* **2010**, *132*, 44-45.

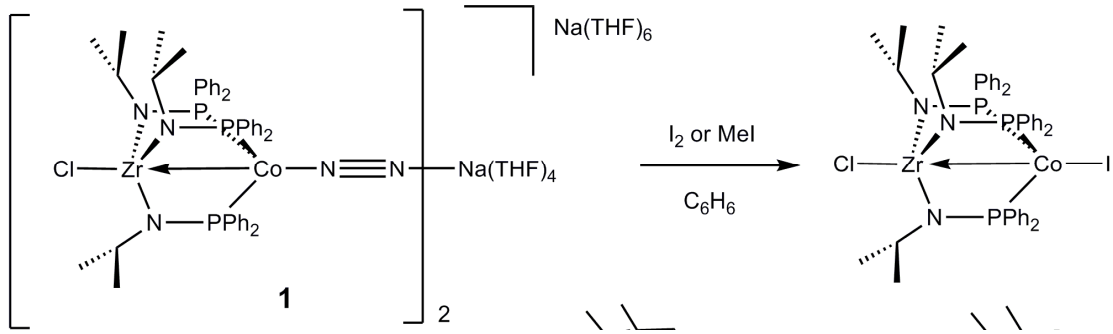
[3] Greenwood, B. P.; Forman, S. I.; Rowe, G. T.; Chen, C.-H, Foxman, B. M.; Thomas, C. M. *Inorg. Chem.* **2009**, *48*, 6251-6260.

(in ppm) were referenced to 85% H_3PO_4. 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. Solution magnetic moments were measured using Evans' method.[4]

Synthesis and identification of [{ClZr(^{i}PrNPPh$_2$)$_3$Co-N$_2$}$_2$(μ-Na(THF)$_4$)][Na(THF)$_6$] (1). A 0.5 % Na/Hg amalgam was prepared from 14.3 g Na (0.62 mmol) and 2.86 g Hg. To this vigorously stirred amalgam in 10 mL THF was added a solution of ICo($Ph_2PN^iPr)_3ZrCl$ (0.258 g, 0.249 mmol) in THF (5 mL). The solution immediately began to change color from green to red. After 2 hours, the resulting red solution was filtered away from the amalgam and the solvent was removed from the filtrate in vacuo. Solvent was extracted back into THF and filtered through Celite. Layering the resulting concentrated red solution with *n*-pentane and cooling to -35 °C resulted in red crystals of **1** (0.175 g, 0.132 mmol, 53.2%). ^{1}H NMR (400 MHz, THF-d_8): δ 7.24 (m, 24H, Ph), 6.83 (m, 12H, Ph), 6.72 (m, 24H, Ph), 3.90 (m, 6H, C*H*$(CH_3)_2$), 3.54 (m, 20H, THF), 1.69 (m, 20H, THF), 1.20 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 18H, CH(C*H*$_3)_2$). ^{31}P{^{1}H} NMR (162 MHz, THF): δ 37 (br s). ^{13}C{^{1}H} NMR (100.5 MHz, THF): δ 144.1 (m, *ipso*-Ph), 132.9 (m, *o*-Ph), 126.2 (s, *m*-Ph), 125.7 (s, *p*-Ph), 67.6 (THF, indistinguishable from solvent), 49.4 (s, *C*H$(CH_3)_2$), 27.0 (s, CH(*CH*$_3)_2$), 25.6 (THF, indistinguishable from solvent). IR (KBr solution cell, THF): 2016 cm^{-1}. UV-vis λ(nm) (ε, M^{-1}cm^{-1}): 459 (34,000), 677 (1400). Repeated attempts and obtaining satisfactory elemental analysis failed as a result of both the lability of N_2 and the extreme oxygen and moisture sensitivity of **1**. Satisfactory X-ray analysis of crystals of **1** could not be obtained to due to rapid loss of solvent upon suspension in paratone N oil. In addition to NMR integration indicating the number of Na-bound THF molecules, the exact identity of **1** was inferred from the following data: (1) Preliminary crystallographic data of a Hf analogue of **1** revealed a Na(THF)$_4$ moiety bridging two complexes through coordination with the distal N_2 nitrogen and an outer sphere Na(THF)$_6$

[4] (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003-2005. (b) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.

countercation;[5] (2) Preliminary results show that reduction of $ICo(Ph_2PN^iPr)_3ZrCl$ with reductants featuring different countercations (Mg^0, Zn^0, etc) lead to significant changes in $\nu(N_2)$.



Reaction of 1 with MeI. Complex **1** (0.050 g, 0.019 mmol) was dissolved in THF (5 mL) and to this was added MeI (2.4 μL, 0.038 mmol) in THF (2 mL). After stirring for 12 hours, volatiles were removed in vacuo. ^{1}H NMR and UV-vis spectra of the remaining solids were identical for those reported for $ICo(Ph_2PN^iPr)_3ZrCl$.[3]

Reaction of 1 with I_2. Complex **1** (0.020 g, 0.0078 mmol) was dissolved in THF (3 mL) and to this was added I_2 (0.0019 g, 0.0075 mmol) in THF (2 mL). After stirring for 4 hours, volatiles were removed in vacuo. ^{1}H NMR and UV-vis spectra of the remaining solids were identical for those reported for $ICo(Ph_2PN^iPr)_3ZrCl$.[3]

$IZr(MesNP^iPr_2)_3CoI$ (3) and $(MesNP^iPr_2)Zr(\mu\text{-}I)(MesNP^iPr_2)_2CoI$ (4). Solid **2** (0.0654 g, 0.0654 mmol) was dissolved in C_6H_6 (5 mL). To this stirring solution, a solution of I_2 (0.0166 g, 0.0654 mmol) in C_6H_6 (2 mL) was added dropwise. The solution immediately changed color from red to greenish-yellow with a yellow precipitate forming as the reaction proceeded over the course of stirring for 1 hour. *n*-Pentane (5 mL) was added and the resulting cloudy yellow/green solution was filtered through a sintered glass frit. The yellow solids collected on the frit were washed with Et_2O (2 x 2 mL), extracted with THF (2 mL), filtered through Celite, and dried in vacuo to obtain **4** as a yellow solid. (0.0390 g, 0.0338, 51.4 %). Crystals suitable for X-ray diffraction were grown via slow diffusion of *n*-pentane into a concentrated CH_2Cl_2 solution at room temp. ^{1}H NMR (400 MHz, THF-d_8): δ 16.2, 7.3, 5.9, 4.7, 3.8,

[5] Setty, V. N.; Greenwood, B. P.; Foxman, B. M.; Thomas, C. M. *manuscript in preparation.*

3.2, 2.8, 2.4, 2.2, 1.9, 1.2, 0.3, -2.0, -9.6. Evans' method (u_{eff}, C_6D_6): 3.00 B.M. UV-vis λ(nm) (ε, $M^{-1}cm^{-1}$): 399 (3700), 705 (140), 743 (200), 949 (120), 1037 (140). Anal. Calcd for $C_{45}H_{75}CoI_2N_3P_3Zr$: C, 46.80; H, 6.55; N, 3.64. Found: C, 46.71; H, 6.53; N, 3.52.

Volatiles were removed from the green *n*-pentane and Et_2O washings from the above procedure. The resulting green solids were extracted into minimal benzene (2 mL), filtered through Celite, and dried in vacuo to obtain **3** as a green solid (0.0282 g, 0.0244 mmol, 37.4%). ^{1}H NMR (400 MHz, C_6D_6): δ 12.7 (iPr-Me), 7.1 (Mes-Me), 2.5 (iPrMe), 1.9 (Mes-Me), -1.9 (Mes-Ar). Evans' method (u_{eff}, C_6D_6): 2.62 B.M. UV-vis λ(nm) (ε, $M^{-1}cm^{-1}$): 394 (4600), 635 (230), 880 (330). Anal. Calcd for $C_{45}H_{75}CoI_2N_3P_3Zr$: C, 46.80; H, 6.55; N, 3.64. Found: C, 46.48; H, 6.31; N, 3.57.

(η^2-MesNP^{i}Pr$_2$)Zr(MesNP^{i}Pr$_2$)$_2$(μ-CH$_3$)CoI (5). To a solution of **2** (0.0474 g, 0.0474 mmol) in C_6H_6 (5 mL) was added a solution of MeI (2.9 μL, 0.0474 mmol) in C_6H_6 (2 mL). The solution, which immediately became green in color, was stirred for 30 minutes. The solution was then filtered through Celite, and volatiles were removed from the filtrate in vacuo to yield analytically pure product as a green powder (0.0355 g, 0.0341 mmol, 67.2%). Crystals suitable for X-ray diffraction were grown via slow diffusion of *n*-pentane into a concentrated benzene solution at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ 9.6 (br s, P_{CoZr}iPr), 7.0 (s, N_{CoZr}Mes), 6.6, 5.9, 4.1, 3.6, 2.4 (s, N_{Zr}Mes), 2.1 (br s, P_{CoZr}iPr), 1.7 (s, N_{CoZr}Mes), 1.6 (s, P_{Zr}iPr), 1.2 (s, N_{Zr}Mes), -0.3 (s, P_{Zr}iPr), -7.0 (br, N_{CoZr}Mes). IR (cm^{-1}): 2730 (C_6H_6 solution); 2727 (KBr pellet). Evans' method (u_{eff}, C_6D_6): 2.99 B.M. UV-vis λ(nm) (ε, $M^{-1}cm^{-1}$): 355 (5100), 655 (140), 905 (210). Anal. Calcd for $C_{46}H_{78}CoIN_3P_3Zr$: C, 52.97; H, 7.54; N, 4.03. Found: C, 52.87; H, 7.37; N, 3.92.

(η^3-P^{i}Pr$_2$N{C$_6$(CH$_3$)$_2$H$_2$(CH$_2$)})Zr(MesNP^{i}Pr$_2$)$_2$CoI (6). A solution of 2-iodopropane (4.3 μL, 0.043 mmol) in C_6H_6 (1 mL) was added dropwise to a stirring solution of **2** (0.0428 g, 0.0428 mmol) in C_6H_6 (5 mL). Bubble formation and a color change from red/brown to green/brown were observed immediately upon addition. The solution was stirred for an additional 15 minutes to ensure complete reaction, and then volatiles were removed in vacuo. The resulting green/brown residue was dissolved in minimal C_6H_6, filtered through Celite, and *n*-pentane was allowed to slowly diffuse into this

concentrated solution overnight, resulting in analytically pure product as dark green/brown crystals (0.0172 g, 0.0167 mmol, 39.2%). A crystal suitable for X-ray diffraction was chosen from this batch of crystals. ^{1}H NMR (400 MHz, C_6D_6): δ 10.4, 8.3, 7.6, 6.5, 2.8, 1.8, 1.3, 1.0, 0.8, -4.3, -5.0, -6.6, -8.2, -17.0, -17.8. Evans' method (u_{eff}, C_6D_6): 3.27 B.M. UV-vis λ(nm) (ε, $M^{-1}cm^{-1}$): 655 (170), 908 (180), 940 (110). Anal. Calcd for $C_{45}H_{74}CoIN_3P_3Zr$: C, 52.62; H, 7.26; N, 4.09. Found: C, 52.70; H, 7.36; N, 3.98.

(η^3-P^{i}Pr$_2$N{C$_6$(CH$_3$)$_2$H$_2$(CH$_2$)})Zr(MesNP^{i}Pr$_2$)$_2$CoCl (7). A solution of cyclohexyl chloride (3.0 μL, 0.026 mmol) in C_6H_6 (1 mL) was added dropwise to a stirring solution of **2** (0.0256 g, 0.0256 mmol) in C_6H_6 (5 mL). Bubble formation and a color change from red/brown to green was observed immediately upon addition. The solution was stirred for an additional 30 minutes to ensure complete reaction, and then volatiles were removed in vacuo. The remaining greenish/brown residue was stirred in *n*-pentane for 15 minutes, at which point the product precipitated as a green powder. Solids were isolated via filtration, resulting in analytically pure product (0.0138 g, 0.0148 mmol, 57.7%). ^{1}H NMR (400 MHz, C_6D_6): δ 13.8, 8.7 (br s, P_{CoZr}iPr), 7.3, 6.4, 2.8 (br s, P_{CoZr}iPr), 1.7, 1.6, 0.5, 0.0, -5.3, -5.5, -6.4, -17.0. Evans' method (u_{eff}, C_6D_6): 3.52 B.M (value is likely falsely high as a result of the poor solubility of this compound in benzene). UV-vis λ(nm) (ε, $M^{-1}cm^{-1}$): 614 (40), 675 (sh), 905 (65). Anal. Calcd for $C_{45}H_{74}CoClN_3P_3Zr$: C, 57.77; H, 7.97; N, 4.49. Found: C, 57.68; H, 8.03; N, 4.60.

Identification of byproducts formed in reaction of 2 with cyclohexylchloride. Complex **2** (5.9 mg, 0.0059 mmol) was dissolved in C_6D_6 (0.5 mL) and transferred to a J. Young tube. To this was added cyclohexylchloride (0.7 μL, 0.006 mmol) in C_6D_6 (0.5 mL). J. Young tube was sealed and shaken for 5 minutes. Volatiles were then vacuum transferred off of the product into another J. Young tube. ^{1}H NMR revealed a large peak at 1.40 ppm corresponding to cyclohexane (see Figure S1).

(MesNH)Zr(MesNP^{i}Pr$_2$)(μ-H)Co(H)(PiPr$_2$H) (8). Solid **2** (0.1942 g, 0.194 mmol) was dissolved in C_6H_6 (15 mL) and transferred to a sealed Schlenk tube. The solution was frozen and the headspace was evacuated and backfilled with H_2 (1 atm). The mixture was thawed and allowed to stir for 12 hours at room temperature. Solvent and volatiles were removed from the resulting red solution in vacuo. The

remaining red solids were dissolved in minimal Et_2O, filtered through Celite, and cooled to -35 °C overnight to provide analytically pure product as red crystals (0.1332 g, 75.9 %). A crystal suitable for X-ray diffraction was chosen from crystals grown in this manner. ^{1}H NMR (400 MHz, C_6D_6): δ 6.4-6.9 (br, 4H, PNMes) 6.7 (s, 2H, NHMes), 4.56 (d, 1H, $^1J_{H\text{-}P}$ = 280 Hz, P*H*^{i}Pr$_2$), 2.69 (m, 4H, $P_{amide}CH(CH_3)_2$), 2.15-2.55 (br m, 12H, PNMes-Me), 2.10 (s, 6H, NHMes-CH_3), 2.05 (s, 3H, NHMes-CH_3), 1.89 (m , 2H, $P_{amide}CH(CH_3)_2$), 1.58 (m, 6H, PH{CH(CH_3)$_2$}), 1.45 (m, 6H, PH{CH(CH_3)$_2$}), 1.30 (m, 12H, $P_{amide}CH(CH_3)_2$), 1.19 (m, 12H, $P_{amide}CH(CH_3)_2$), -9.13 (br m, 1H, Co-$H_{bridging}$), -17.98 (dt, $^2J_{H\text{-}P}$ = 60 Hz, 48 Hz, 1H, Co-$H_{terminal}$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 77.7 (s, 2P), 57.5 (s, 1P). ^{31}P NMR (162 MHz, C_6D_6): δ 77.7 (s, 2P), 57.5 (d, $^1J_{H\text{-}P}$ = 288 Hz, 1P). ^{13}C{^{1}H} NMR: δ 150.4 (*ipso*-NMes), 148.8 (*ipso*-PNMes), 137.9 (*o*-NMes), 134.0 (*o*-PNMes), 132.2 (*m*-NMes), 129.6 (*m*-PNMes), 124.8 (*p*-NMes), 120.5 (*p*-PNMes), 32.7 (m, PH{*C*H(CH_3)$_2$), 31.2 (m, $P_{amide}CH(CH_3)_2$), 25.7 (m, NMes-Me), 23.5 (s, PH{CH(*C*H$_3$)$_2$), 23.0 (s, $P_{amide}CH(CH_3)_2$), 21.4 (s, PH{CH(*C*H$_3$)$_2$), 21.0 (s, $P_{amide}CH(CH_3)_2$), 20.3 (s, NMes-Me), 19.2 (s, PNMes-Me), 18.8 (s, PNMes-Me). IR (cm^{-1}, KBr pellet): 3345 (N-H), 2231 (P-H), 1610 (Co-H). UV-vis λ(nm) (ε, M^{-1}cm^{-1}): 291 (16000), 357 (4000), 675 (45). Anal. Calcd for $C_{45}H_{79}CoN_3P_3Zr$: C, 59.71; H, 8.80; N, 4.64. Found: C, 59.77; H, 8.74; N, 4.64.

X-ray Crystallography Procedures. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[6] Preliminary cell constants were obtained from three sets of 12 frames. Crystallographic parameters are summarized in Table S1, and further experimental crystallographic details are described for each compound on pages S27-S38. Data in CIF format are also provided in a separate file.

Table S1. Crystallographic Data and Refinement Parameters for complexes **4**-**8**.

	4	**5**·C_6H_6	**6**	**7**·***n*-pentane**	**8**
chemical formula	$C_{45}H_{75}CoI_2N_3P_3Zr$	$C_{52}H_{54}CoIN_3P_3Zr$	$C_{45}H_{74}CoIN_3P_3Zr$	$C_{50}H_{86}ClCoN_3P_3Zr$	$C_{45}H_{79}CoN_3P_3Zr$
fw	1154.99	1124.67	1027.08	1021.32	905.22
T (K)	120	120	120	120	100
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
a (Å)	27.2429(12)	10.0365(4)	12.6346(10)	12.2227(5)	11.4036(3)
b (Å)	31.7135(14	15.6058(7)	29.449(2)	14.2597(7)	12.3007(3)
c (Å)	16.8195(7)	18.1449(8)	13.3675(10)	18.3302(9)	18.7536(5)
α (°)	90	83.098	90	77.154(3)	94.3420(10)
β (°)	127.715(2)	74.691(2)	106.141(4)	82.246(2)	105.8890(10)
γ (°)	90	85.221(2)	90	79.036(2)	108.4810(10)
V (Å^3)	11495.3(9)	2717.3(2)	4777.7(6)	3043.6(2)	2361.24(11)
space group	*C2/c*	*P-1*	*P12$_1$/n1*	*P-1*	*P-1*
Z	8	2	4	2	2
D_{calc} (g/cm^3)	1.335	1.374	1.428	1.114	1.273
μ (cm^{-1})	16.56	12.06	13.45	6.65	7.06
R1, wR2[a] (I > 2σ(I))	0.0228, 0.0515	0.0185, 0.0454	0.0322, 0.0819	0.0669, 0.1773	0.0272, 0.0612

[6]Apex2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, June 2006.

Computational Details. All calculations were performed using Gaussian03-E.01[7] for the Linux operating system. Density functional theory calculations were carried out using a combination of Becke's 1988 gradient-corrected exchange functional[8] and Perdew's 1986 electron correlation functional[9] (BP86). A mixed-basis set was employed, using the LANL2TZ(f) triple zeta basis set with effective core potentials for iodine, cobalt, and zirconium,[10] Gaussian03's internal 6-311++G(d,p) for heteroatoms (nitrogen, phosphorus, and oxygen) and the methyl groups directly bound to metal centers, and Gaussian03's internal LANL2DZ basis set (equivalent to D95V[11]) for all other carbon and hydrogen atoms. Starting with crystallographically determined geometries as a starting point (when available), the geometries were optimized to a minimum, followed analytical frequency calculations to confirm that no imaginary frequencies were present.

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[11] Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1976; Vol. 3, p 1-28.

Table S2. Computationally optimized structural parameters for **3**

Atom	X	Y	Z	Atom	X	Y	Z
Zr1	0.57508	-0.00145	-0.00452	H66	-1.04715	-4.07743	3.91397
Co2	-2.08968	0.00252	0.01116	H67	-1.93542	-2.75430	4.70441
P3	-1.26985	-0.61674	2.18686	H68	2.82492	1.65340	5.61848
P4	-1.28215	2.19791	-0.54770	H69	3.81572	-2.43012	4.57891
P5	-1.29482	-1.57562	-1.62061	H70	0.16240	2.23814	4.65756
N6	0.42471	-0.34334	2.13213	H71	1.58521	2.95497	3.86468
N7	0.41090	2.02101	-0.77341	H72	0.35090	2.11041	2.88469
N8	0.40116	-1.67859	-1.37051	H73	4.59735	-1.39898	6.81903
C9	-2.04628	0.38107	3.62006	H74	5.51926	-0.19267	5.88664
C10	-3.59393	0.28334	3.68659	H75	4.33534	0.34705	7.10666
C11	-1.47788	0.09600	5.04360	H76	2.85496	-3.52638	2.84410
C12	-1.58263	-2.45737	2.54962	H77	2.32026	-2.50961	1.47955
C13	-3.03012	-2.91507	2.22680	H78	1.11580	-3.22126	2.57991
C14	-1.15780	-2.97520	3.95204	H79	-1.81428	2.17195	-2.88127
C15	1.41174	-0.36920	3.20037	H80	-4.00839	3.26308	-3.07051
C16	1.66126	0.79177	4.00487	H81	-3.94139	3.86152	-1.39406
C17	2.65880	0.75036	5.01403	H82	-4.10831	2.11204	-1.70104
C18	3.44160	-0.39868	5.25866	H83	-1.76644	4.44473	-3.66634
C19	3.20650	-1.52715	4.43595	H84	-2.00443	5.13710	-2.04705
C20	2.22924	-1.53228	3.41186	H85	-0.42891	4.42014	-2.47993
C21	0.89490	2.09303	3.84031	H86	-0.90746	3.01209	1.63753
C22	4.52572	-0.41176	6.32631	H87	-3.38434	2.34551	1.59407
C23	2.11755	-2.76336	2.53615	H88	-3.06384	3.91590	2.40392
C24	-2.07592	2.93538	-2.12213	H89	-3.75125	3.86942	0.75868
C25	-3.62351	3.03577	-2.05637	H90	-0.21741	5.00178	0.06126
C26	-1.51741	4.31231	-2.59444	H91	-1.05666	5.42649	1.58297
C27	-1.58705	3.43185	0.86714	H92	-1.94990	5.44376	0.04472
C28	-3.03042	3.37767	1.43533	H93	2.77855	4.04305	-4.26697

C29	-1.16855	4.90641	0.61054	H94	3.80022	5.18984	-0.22015
C30	1.38760	2.96460	-1.29427	H95	5.31925	5.80399	-2.19286
C31	1.62603	3.07963	-2.70389	H96	4.01550	6.77707	-2.92023
C32	2.61710	3.97659	-3.18165	H97	4.77489	5.46683	-3.86244
C33	3.39924	4.77215	-2.31635	H98	2.85934	4.22960	1.60547
C34	3.18210	4.61771	-0.92543	H99	1.11942	3.84619	1.49027
C35	2.21179	3.73070	-0.40032	H100	2.32406	2.53929	1.40704
C36	0.85911	2.27612	-3.73974	H101	-1.80520	-3.59245	-0.43767
C37	4.43275	5.75232	-2.85132	H102	-4.00930	-4.30157	-1.25136
C38	2.11758	3.58203	1.10425	H103	-4.11029	-2.54060	-0.93784
C39	-2.08344	-3.31030	-1.47218	H104	-3.96787	-3.14901	-2.60887
C40	-3.63271	-3.30842	-1.56784	H105	-1.78913	-5.39679	-2.03565
C41	-1.53533	-4.39837	-2.44468	H106	-2.02519	-4.32053	-3.43008
C42	-1.61700	-0.96154	-3.39170	H107	-0.44701	-4.35763	-2.59841
C43	-3.06832	-0.46046	-3.61864	H108	-0.95065	-0.07436	-3.41061
C44	-1.19008	-1.90782	-4.54840	H109	-3.11585	0.10871	-4.56875
C45	1.37515	-2.60264	-1.93032	H110	-3.42433	0.18886	-2.80160
C46	1.61514	-3.88080	-1.32508	H111	-3.77896	-1.30145	-3.70101
C47	2.60648	-4.74209	-1.86370	H112	-0.23584	-2.42653	-4.35945
C48	3.38692	-4.39023	-2.98656	H113	-1.96616	-2.67004	-4.73867
C49	3.16680	-3.10965	-3.54951	H114	-1.08020	-1.31685	-5.47963
C50	2.19601	-2.21216	-3.04323	H115	2.76972	-5.71475	-1.37821
C51	0.85011	-4.37698	-0.11037	H116	3.78240	-2.78535	-4.39962
C52	4.42060	-5.34317	-3.56836	H117	0.10234	-5.14464	-0.38822
C53	2.09985	-0.83528	-3.66738	H118	1.53839	-4.84112	0.61827
H54	-1.78027	1.41872	3.33752	H119	0.32350	-3.54928	0.38680
H55	-3.96850	1.05069	4.39311	H120	5.29492	-4.79650	-3.96667
H56	-4.08567	0.43995	2.71286	H121	4.78286	-6.05913	-2.80859
H57	-3.91446	-0.70097	4.07381	H122	3.99514	-5.93481	-4.40379
H58	-1.71903	0.95715	5.69839	H123	2.79463	-0.74621	-4.52195
H59	-0.38969	-0.06105	5.07128	H124	2.36960	-0.05422	-2.93228
H60	-1.96452	-0.78996	5.48543	H125	1.08392	-0.60923	-4.02840
H61	-0.91059	-2.91835	1.79656	H126	0.32731	1.43643	-3.26909

H62	-3.07124	-4.02291	2.21902	H127	0.11588	2.90250	-4.26970
H63	-3.74703	-2.56281	2.98909	H128	1.54699	1.87040	-4.50283
H64	-3.38330	-2.54339	1.25067	I129	-4.69695	0.00512	0.02811
H65	-0.20442	-2.54878	4.30529	I130	3.41992	-0.00294	-0.01587

Table S3. Computationally optimized structural parameters for **4**

Atom	X	Y	Z	Atom	X	Y	Z
Zr1	0.23158	0.24257	0.33537	H66	-3.43626	-4.55162	-0.84171
Co2	-2.54820	-0.51508	0.15638	H67	-3.97565	-2.90642	-1.26340
P3	-1.23362	-2.35044	-0.22408	H68	-3.70659	-4.12545	-2.55273
P4	-2.12126	1.29759	-1.21736	H69	-1.32809	-4.79816	-3.28068
P5	1.98938	1.62626	1.95025	H70	-1.30064	-5.47064	-1.63539
N6	0.39144	-1.79171	-0.44854	H71	0.05386	-4.45702	-2.19960
N7	-0.44455	1.75263	-1.00374	H72	-0.47129	-3.03255	1.91750
N8	2.34237	0.23697	0.99756	H73	-2.87783	-2.58218	2.36729
C9	1.47155	-2.62209	-0.94244	H74	-2.43732	-4.22675	2.93187
C10	1.70981	-2.71374	-2.35615	H75	-3.37482	-4.00169	1.42455
C11	2.76182	-3.53054	-2.84187	H76	0.17920	-5.03626	0.35430
C12	3.60108	-4.27123	-1.97847	H77	-1.51585	-5.58719	0.51462
C13	3.37930	-4.14034	-0.58686	H78	-0.48366	-5.47938	1.95845
C14	2.34733	-3.33027	-0.05178	H79	1.89751	4.38339	-4.08204
C15	0.85906	-1.97308	-3.37902	H80	0.83609	6.18453	-0.28929
C16	4.69946	-5.17477	-2.51958	H81	1.85933	1.86874	-4.15984
C17	2.22981	-3.24141	1.46082	H82	0.14453	2.12114	-4.55185
C18	-1.83665	-3.33337	-1.75061	H83	0.59603	0.99686	-3.24290
C19	-3.32801	-3.73992	-1.58503	H84	2.63869	7.24231	-1.86477
C20	-1.03786	-4.58152	-2.23244	H85	2.76847	6.61632	-3.53505
C21	-1.21014	-3.54095	1.26534	H86	1.30430	7.49329	-3.01727
C22	-2.55651	-3.58302	2.03640	H87	0.23169	4.55992	1.58502
C23	-0.71885	-4.98884	0.99223	H88	-1.35617	4.77848	0.81250
C24	0.17856	2.99030	-1.42938	H89	-0.74854	3.13454	1.16057
C25	0.80521	3.10156	-2.71670	H90	-2.94815	2.95428	0.28543
C26	1.42050	4.32385	-3.09372	H91	-3.41611	4.97206	-0.94375
C27	1.44008	5.45656	-2.24793	H92	-3.46569	4.15032	-2.51882
C28	0.83369	5.32546	-0.97541	H93	-1.90189	4.40203	-1.69795

C29	0.21040	4.12732	-0.54564	H94	-4.99194	1.57231	-0.30775
C30	0.85045	1.95573	-3.71629	H95	-5.04461	2.35560	-1.91844
C31	2.07462	6.76744	-2.68889	H96	-5.29018	3.33118	-0.44704
C32	-0.45183	4.13841	0.82437	H97	-1.49556	0.31842	-3.30211
C33	-3.20285	2.81191	-0.78446	H98	-2.50315	1.66163	-5.07812
C34	-2.96044	4.15460	-1.53815	H99	-1.85492	2.84552	-3.90053
C35	-4.71830	2.48064	-0.86865	H100	-3.60468	2.48784	-3.94946
C36	-2.42436	0.86743	-3.04373	H101	-3.66306	-0.50188	-4.22183
C37	-2.59737	2.04307	-4.04148	H102	-4.57850	0.36112	-2.94971
C38	-3.61380	-0.12348	-3.18085	H103	-3.51763	-0.98591	-2.49905
C39	3.64647	-0.23959	0.60336	H104	5.40335	-0.60113	-2.35543
C40	3.95043	-0.20105	-0.80181	H105	6.66745	-1.50562	1.68341
C41	5.20726	-0.63946	-1.27510	H106	2.03090	-0.26209	-1.82697
C42	6.21175	-1.12168	-0.40239	H107	3.36955	0.34248	-2.81633
C43	5.90831	-1.14158	0.97712	H108	2.65225	1.38441	-1.55497
C44	4.65989	-0.71134	1.50147	H109	8.19490	-1.98826	-0.11941
C45	2.95018	0.34747	-1.79473	H110	8.11565	-0.75475	-1.40807
C46	7.56118	-1.58605	-0.92992	H111	7.44444	-2.37871	-1.69385
C47	4.48136	-0.79584	3.00805	H112	5.35895	-1.28304	3.46869
C48	1.98279	1.37975	3.85403	H113	3.58581	-1.37406	3.28628
C49	1.05650	2.46456	4.48332	H114	4.38037	0.20120	3.47435
C50	1.53404	-0.03180	4.33254	H115	3.02179	1.56499	4.19816
C51	3.48372	2.79635	1.75434	H116	1.35318	3.49677	4.23127
C52	3.75123	3.19969	0.28460	H117	1.07354	2.36825	5.58689
C53	3.40824	4.06401	2.64761	H118	0.01407	2.32064	4.14672
H54	2.92031	-3.58972	-3.92820	H119	2.15566	-0.36721	5.18412
H55	4.03995	-4.67090	0.11298	H120	1.60973	-0.79312	3.53719
H56	0.18577	-1.24973	-2.89101	H121	0.48150	-0.01424	4.66258
H57	0.23297	-2.67698	-3.96127	H122	4.34322	2.18186	2.10337
H58	1.49701	-1.43201	-4.10310	H123	2.87674	3.69721	-0.16910
H59	4.94078	-4.93367	-3.57053	H124	4.03304	2.33141	-0.32869
H60	5.62751	-5.08311	-1.92498	H125	4.59864	3.91319	0.25507
H61	4.39522	-6.23998	-2.48562	H126	3.39317	3.83293	3.72658

H62	1.62577	-4.06913	1.87688	H127	4.30547	4.68482	2.45690
H63	1.76514	-2.29115	1.76913	H128	2.52241	4.68107	2.40547
H64	3.23236	-3.30477	1.91893	I129	-1.65872	0.39424	2.52077
H65	-1.77760	-2.56009	-2.54351	I130	-5.03846	-1.01770	0.65079

Table S4. Computationally optimized structural parameters for **5**

Atom	X	Y	Z	Atom	X	Y	Z
Zr1	0.09119	0.23557	0.44492	H68	-4.00394	-4.01601	-2.17113
Co2	-2.52830	-0.52193	0.52450	H69	-1.69409	-4.65638	-3.19890
P3	-1.28276	-2.35237	-0.06470	H70	-1.45793	-5.39701	-1.59957
P4	-2.33436	1.28844	-0.90989	H71	-0.20158	-4.32454	-2.27150
P5	1.79569	1.60667	2.18088	H72	-0.30318	-3.11962	1.95636
N6	0.29996	-1.77033	-0.42035	H73	-2.65173	-2.68447	2.67752
N7	-0.67440	1.79765	-0.80702	H74	-2.15056	-4.34400	3.13824
N8	2.19834	0.27368	1.17316	H75	-3.24567	-4.07233	1.74970
C9	1.35942	-2.55530	-1.01748	H76	0.18303	-5.04666	0.26859
C10	1.50380	-2.58428	-2.44735	H77	-1.49082	-5.61207	0.55910
C11	2.54148	-3.34784	-3.03754	H78	-0.32811	-5.56751	1.90416
C12	3.45960	-4.09604	-2.26435	H79	1.51616	4.48168	-3.94706
C13	3.33185	-4.02475	-0.85740	H80	0.55955	6.24310	-0.10781
C14	2.31658	-3.26834	-0.21931	H81	1.52826	1.93310	-3.99993
C15	0.56763	-1.82180	-3.37477	H82	-0.18623	2.19929	-4.38792
C16	4.53769	-4.94773	-2.91879	H83	0.25973	1.07676	-3.07488
C17	2.30905	-3.23998	1.30060	H84	2.12565	7.42705	-1.69986
C18	-2.04320	-3.26834	-1.55552	H85	2.50258	6.70652	-3.29307
C19	-3.50372	-3.69530	-1.23575	H86	0.93218	7.50438	-3.02100
C20	-1.28744	-4.47669	-2.18289	H87	0.01897	4.65001	1.76076
C21	-1.11189	-3.59995	1.36942	H88	-1.61261	4.72449	1.05373
C22	-2.36474	-3.67230	2.28184	H89	-0.85423	3.13992	1.38742
C23	-0.65266	-5.03338	0.98816	H90	-3.18068	2.89596	0.64349
C24	-0.09726	3.04823	-1.24947	H91	-3.77134	4.90280	-0.56271
C25	0.48727	3.17709	-2.55499	H92	-3.81149	4.08654	-2.14102
C26	1.07122	4.40970	-2.94448	H93	-2.24698	4.39848	-1.34574
C27	1.10231	5.53779	-2.09197	H94	-5.18403	1.42051	0.06564
C28	0.54207	5.38970	-0.80061	H95	-5.32856	2.28015	-1.50362
C29	-0.05022	4.17943	-0.36008	H96	-5.55507	3.16859	0.02374

C30	0.52127	2.03080	-3.55384	H97	-1.83106	0.28432	-3.00743
C31	1.70067	6.86046	-2.54833	H98	-2.89773	1.61910	-4.74908
C32	-0.65809	4.16240	1.03491	H99	-2.20199	2.80856	-3.60495
C33	-3.46289	2.75104	-0.41928	H100	-3.95408	2.45761	-3.58666
C34	-3.29167	4.10732	-1.16819	H101	-4.00872	-0.58565	-3.79246
C35	-4.96724	2.36409	-0.46147	H102	-4.90051	0.36649	-2.57105
C36	-2.74370	0.84169	-2.71086	H103	-3.84913	-0.96309	-2.04411
C37	-2.95244	2.00818	-3.71240	H104	5.24429	-0.30381	-2.24863
C38	-3.94372	-0.14407	-2.77766	H105	6.59502	-1.32649	1.73379
C39	3.51347	-0.12993	0.74371	H106	1.90956	-0.16409	-1.73946
C40	3.79793	-0.02222	-0.66292	H107	3.19989	0.65797	-2.63113
C41	5.06372	-0.39470	-1.16861	H108	2.36924	1.50468	-1.29653
C42	6.09655	-0.87587	-0.32918	H109	8.14582	-1.58877	-0.09204
C43	5.81318	-0.96272	1.05243	H110	7.92553	-0.43949	-1.44189
C44	4.55589	-0.60362	1.60781	H111	7.35839	-2.11933	-1.60524
C45	2.76485	0.52529	-1.62459	H112	5.33354	-1.13569	3.55723
C46	7.45191	-1.27647	-0.89289	H113	3.60262	-1.51585	3.34794
C47	4.38962	-0.77943	3.10789	H114	4.11569	0.16097	3.61612
C48	1.78364	1.26384	4.07586	H115	2.80576	1.48856	4.44715
C49	0.79060	2.26039	4.74685	H116	1.00001	3.31671	4.50488
C50	1.41114	-0.19243	4.47639	H117	0.83795	2.15009	5.84831
C51	3.24772	2.83390	2.05895	H118	-0.24598	2.04084	4.43254
C52	3.49418	3.31630	0.60851	H119	1.98656	-0.50945	5.36667
C53	3.11157	4.05186	3.01165	H120	1.61712	-0.91544	3.66828
H54	2.62681	-3.35711	-4.13375	H121	0.33859	-0.26300	4.72956
H55	4.05557	-4.55945	-0.22651	H122	4.13357	2.24279	2.38089
H56	-0.09209	-1.14763	-2.80562	H123	2.59887	3.80003	0.17975
H57	-0.07522	-2.51424	-3.95289	H124	3.80297	2.48800	-0.04684
H58	1.14085	-1.22254	-4.10727	H125	4.31401	4.06208	0.60851
H59	4.84219	-4.53460	-3.89787	H126	3.08487	3.76577	4.07746
H60	5.43804	-5.01967	-2.28169	H127	3.98759	4.71488	2.87014
H61	4.17846	-5.98142	-3.09615	H128	2.20680	4.64694	2.78377
H62	1.76151	-4.10243	1.72540	I129	-4.94357	-1.00194	1.37756

H63	1.84514	-2.31487	1.67916	C130	-1.31436	0.17783	2.29246
H64	3.34465	-3.28893	1.68053	H131	-1.24127	1.21120	2.67058
H65	-2.07849	-2.45754	-2.31153	H132	-0.71924	-0.47555	2.95378
H66	-3.51981	-4.55614	-0.54146	H133	-2.37278	-0.11551	2.49624
H67	-4.10239	-2.88756	-0.77930				

Table S5. Computationally optimized structural parameters for $MeZr(MesNP^{i}Pr_2)_3CoI$

Atom	X	Y	Z	Atom	X	Y	Z
Zr1	0.85121	-0.00325	-0.01229	H68	3.15516	0.10329	5.84936
Co2	-1.87874	0.00664	0.02005	H69	4.22293	-3.42124	3.57340
P3	-1.01119	-1.13002	1.96379	H70	0.44986	0.88784	5.17314
P4	-1.01895	2.26280	0.01383	H71	1.83987	1.83882	4.59833
P5	-1.05466	-1.12171	-1.94945	H72	0.58854	1.29664	3.43989
N6	0.68310	-0.82981	1.98465	H73	5.05506	-3.10382	6.00077
N7	0.67100	2.13760	-0.28858	H74	5.90408	-1.62892	5.47309
N8	0.64143	-1.31393	-1.72369	H75	4.74619	-1.54815	6.82739
C9	-1.77823	-0.55493	3.61541	H76	3.24741	-3.93693	1.58049
C10	-3.32847	-0.62134	3.64747	H77	2.52353	-2.60768	0.63804
C11	-1.22663	-1.24338	4.89938	H78	1.47669	-3.71080	1.55597
C12	-1.28183	-3.00843	1.83691	H79	-1.53280	2.88544	-2.23616
C13	-2.74274	-3.39153	1.47886	H80	-3.74235	3.96261	-2.13886
C14	-0.76805	-3.88270	3.01459	H81	-3.70666	4.04178	-0.35881
C15	1.69842	-1.13788	2.97257	H82	-3.82984	2.45847	-1.16765
C16	1.95247	-0.26533	4.08336	H83	-1.52362	5.29896	-2.33710
C17	2.98907	-0.57775	5.00245	H84	-1.76068	5.48536	-0.58562
C18	3.81230	-1.71615	4.86039	H85	-0.18077	4.93827	-1.21103
C19	3.58188	-2.54333	3.73362	H86	-0.61475	2.43354	2.32901
C20	2.56420	-2.27187	2.78810	H87	-3.12902	1.96060	2.10583
C21	1.16101	1.00780	4.33376	H88	-2.72285	3.21029	3.33005
C22	4.93388	-2.01608	5.84413	H89	-3.38715	3.68293	1.74427
C23	2.44294	-3.17952	1.57993	H90	0.21069	4.73379	1.34689
C24	-1.81335	3.40179	-1.29673	H91	-0.59720	4.77054	2.94338
C25	-3.36280	3.45471	-1.22963	H92	-1.48694	5.27332	1.48764
C26	-1.26958	4.86044	-1.35124	H93	3.09213	5.01814	-3.07340
C27	-1.25841	3.09197	1.70861	H94	4.23994	4.80529	1.09516

C28	-2.70900	2.97098	2.24765	H95	5.74691	5.94520	-0.62550
C29	-0.74405	4.54982	1.86690	H96	4.48592	7.14510	-1.00714
C30	1.67898	3.15052	-0.53292	H97	5.17835	6.14325	-2.30965
C31	1.90849	3.67718	-1.84821	H98	3.29840	3.32866	2.55171
C32	2.94130	4.62922	-2.05625	H99	1.52251	3.21309	2.41286
C33	3.77971	5.08032	-1.01315	H100	2.54225	1.85736	1.88624
C34	3.57873	4.51108	0.26844	H101	-1.54459	-3.38673	-1.36348
C35	2.56520	3.55676	0.52499	H102	-3.77058	-3.85096	-2.28990
C36	1.09783	3.25310	-3.06166	H103	-3.85169	-2.25416	-1.47985
C37	4.85545	6.12926	-1.25289	H104	-3.76508	-2.35410	-3.25705
C38	2.47393	2.95951	1.91546	H105	-1.57355	-4.66903	-3.41364
C39	-1.84717	-2.82858	-2.27149	H106	-1.83069	-3.23766	-4.43518
C40	-3.39827	-2.80727	-2.31834	H107	-0.23704	-3.50915	-3.67783
C41	-1.32329	-3.59465	-3.52248	H108	-0.69896	0.81143	-3.25083
C42	-1.33083	-0.06507	-3.50702	H109	-2.82739	1.26313	-4.39262
C43	-2.79160	0.44029	-3.65057	H110	-3.20644	0.80913	-2.69684
C44	-0.82343	-0.64129	-4.85829	H111	-3.46083	-0.35994	-4.01390
C45	1.64019	-2.03221	-2.49106	H112	0.13820	-1.17361	-4.77156
C46	1.87585	-3.43398	-2.29186	H113	-1.56304	-1.33653	-5.29268
C47	2.90379	-4.08653	-3.02251	H114	-0.69272	0.18741	-5.58295
C48	3.73038	-3.40636	-3.94381	H115	3.06035	-5.16122	-2.85177
C49	3.52193	-2.01304	-4.09169	H116	4.17246	-1.44256	-4.76885
C50	2.51366	-1.31722	-3.38261	H117	0.34582	-4.92334	-1.82846
C51	1.07848	-4.27607	-1.30983	H118	1.75025	-4.93968	-0.73566
C52	4.79999	-4.13564	-4.74323	H119	0.52898	-3.63871	-0.60126
C53	2.41589	0.18545	-3.55653	H120	5.67921	-3.49070	-4.92502
H54	-1.48499	0.51342	3.63433	H121	5.14595	-5.04557	-4.22012
H55	-3.69041	-0.08039	4.54474	H122	4.41428	-4.45100	-5.73354
H56	-3.80216	-0.17466	2.75828	H123	3.16186	0.54237	-4.28935
H57	-3.68352	-1.66468	3.72879	H124	2.60518	0.71340	-2.60369
H58	-1.46212	-0.60565	5.77492	H125	1.41813	0.49648	-3.90559
H59	-0.14000	-1.41711	4.88357	H126	0.52917	2.33502	-2.85224
H60	-1.72750	-2.21283	5.06427	H127	0.38076	4.03849	-3.36786

H61	-0.65217	-3.22729	0.94908	H128	1.76260	3.06466	-3.92420
H62	-2.77722	-4.44835	1.14571	I129	-4.49412	0.01419	0.04416
H63	-3.40994	-3.30013	2.35438	C130	3.14529	-0.01617	-0.01512
H64	-3.16113	-2.75703	0.67899	H131	3.55467	0.94560	-0.37787
H65	0.19702	-3.54016	3.42328	H132	3.56080	-0.18670	0.99548
H66	-0.64207	-4.92754	2.66603	H133	3.54860	-0.81013	-0.67161
H67	-1.50227	-3.90389	3.83894				

Figure S1. ^{1}H NMR spectrum of **4.**

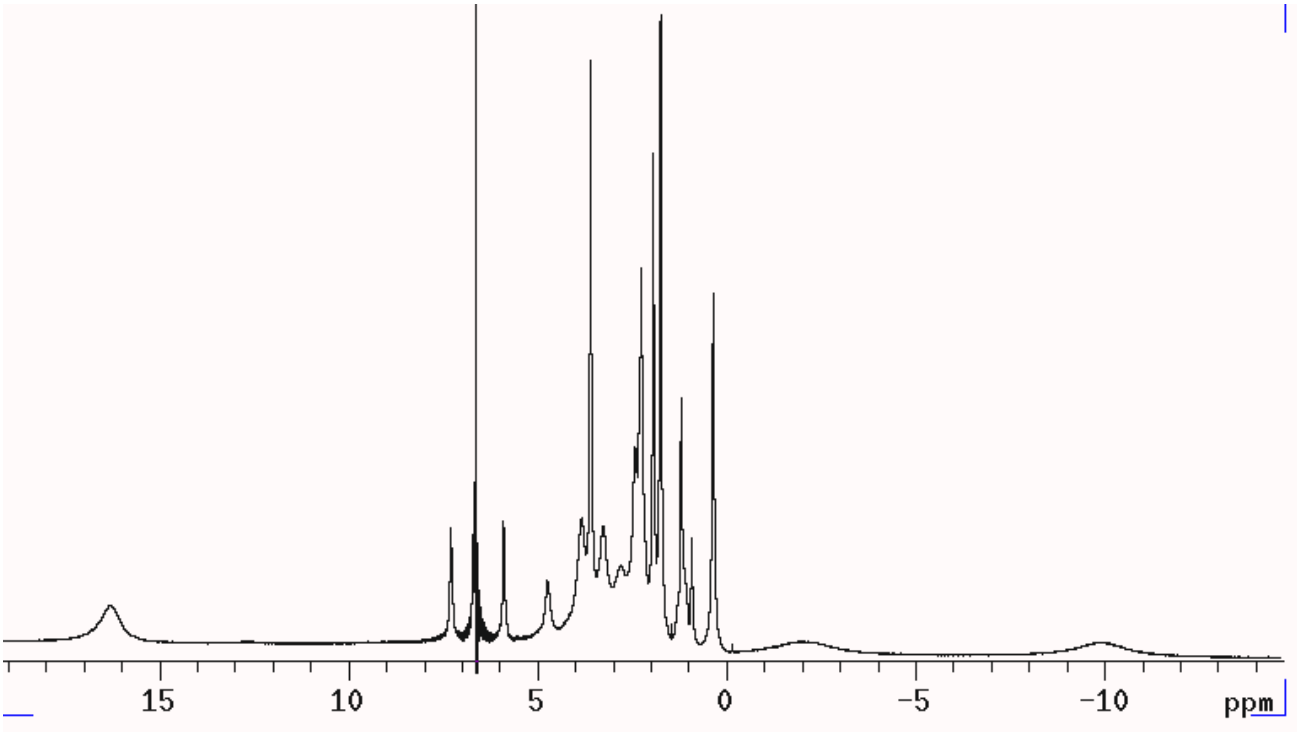


Figure S2. ^{1}H NMR spectrum of **5.**

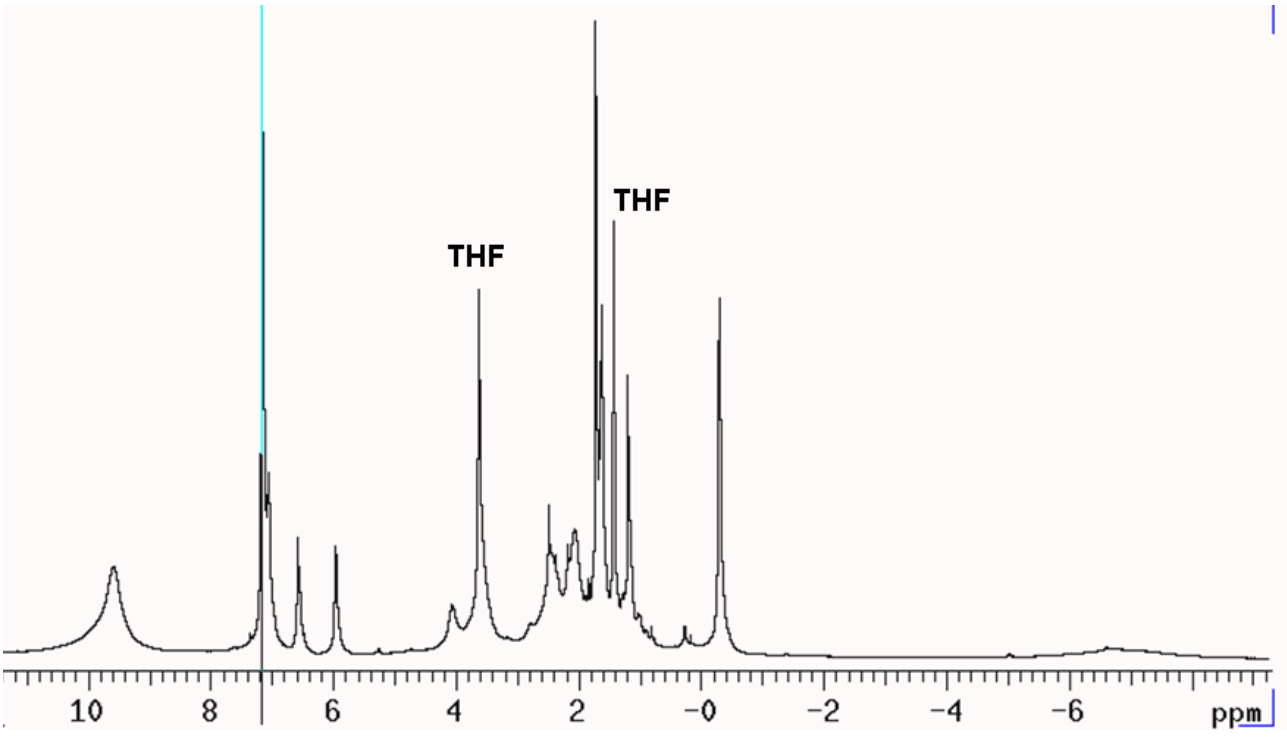


Figure S3. ^{1}H NMR spectrum of **6**.

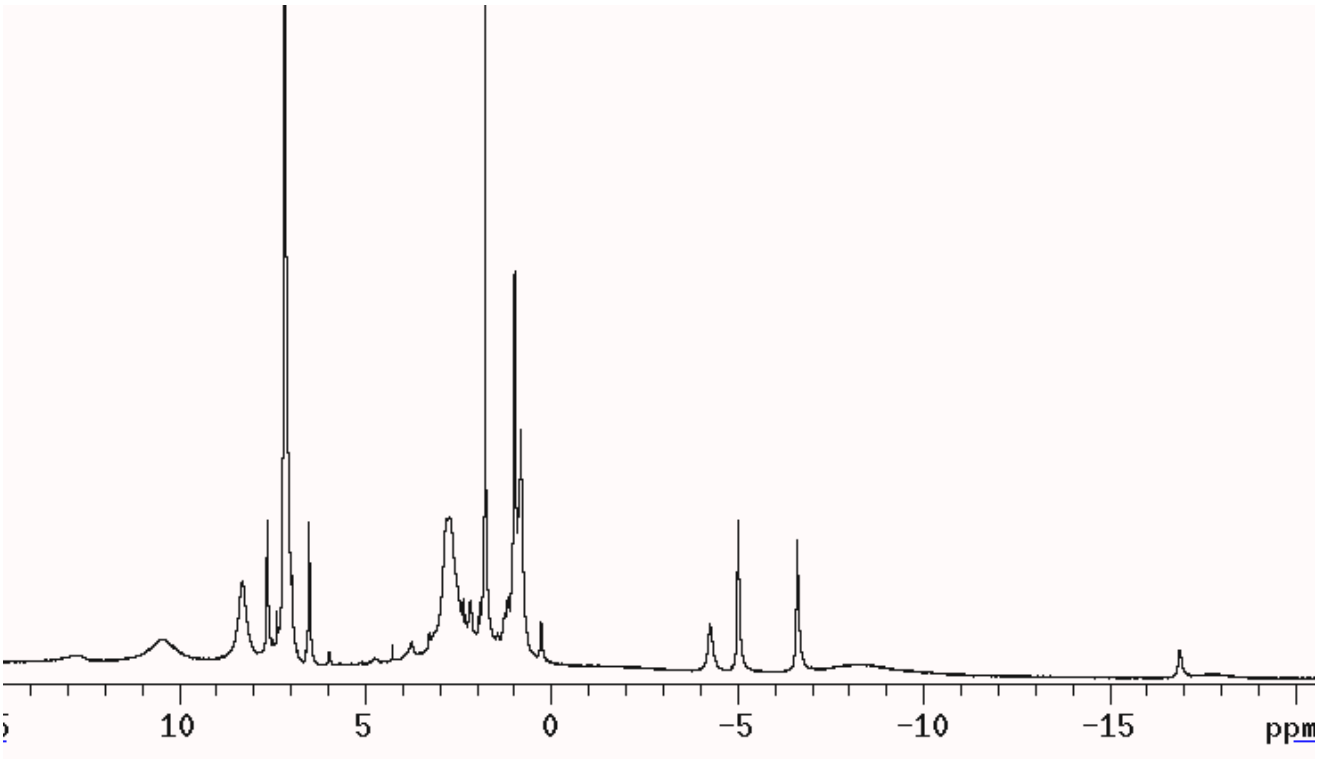


Figure S4. ^{1}H NMR spectrum of **7**.

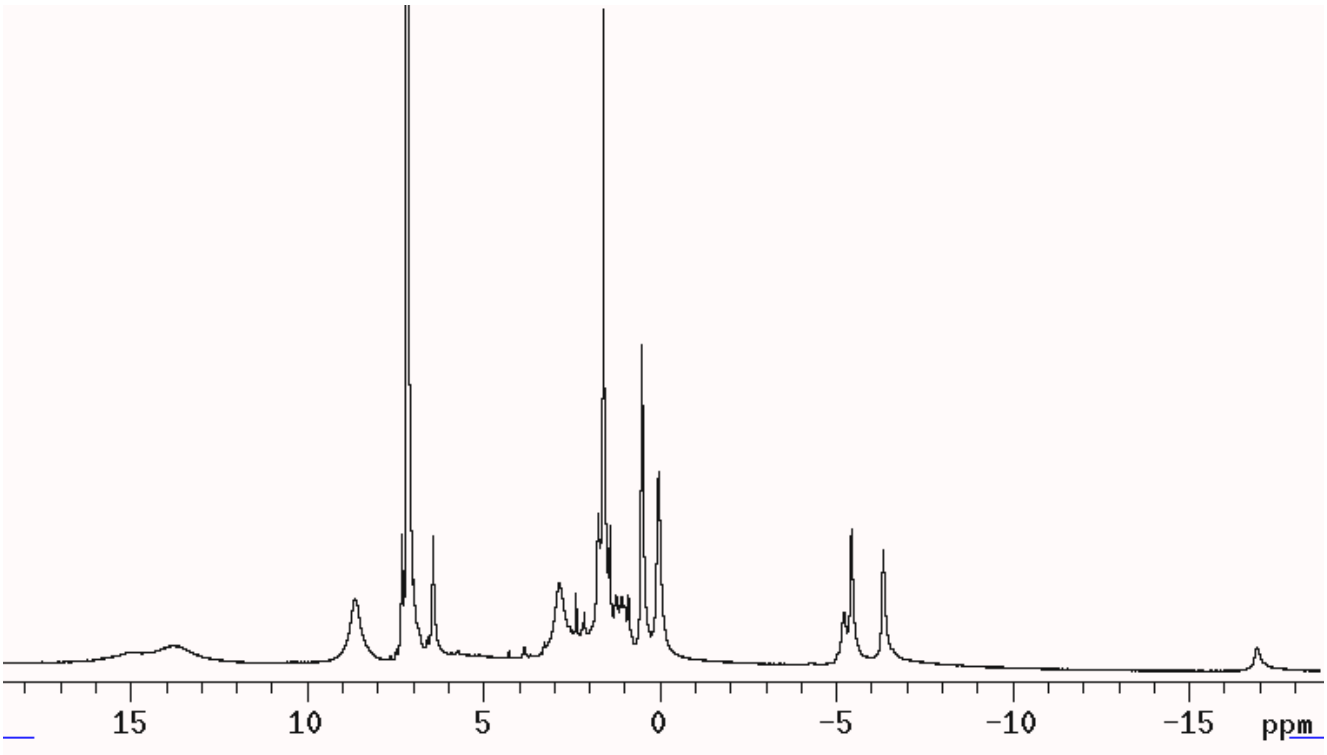


Figure S5. ^{1}H NMR spectrum of the volatiles from the reaction of **2** with cyclohexylchloride.

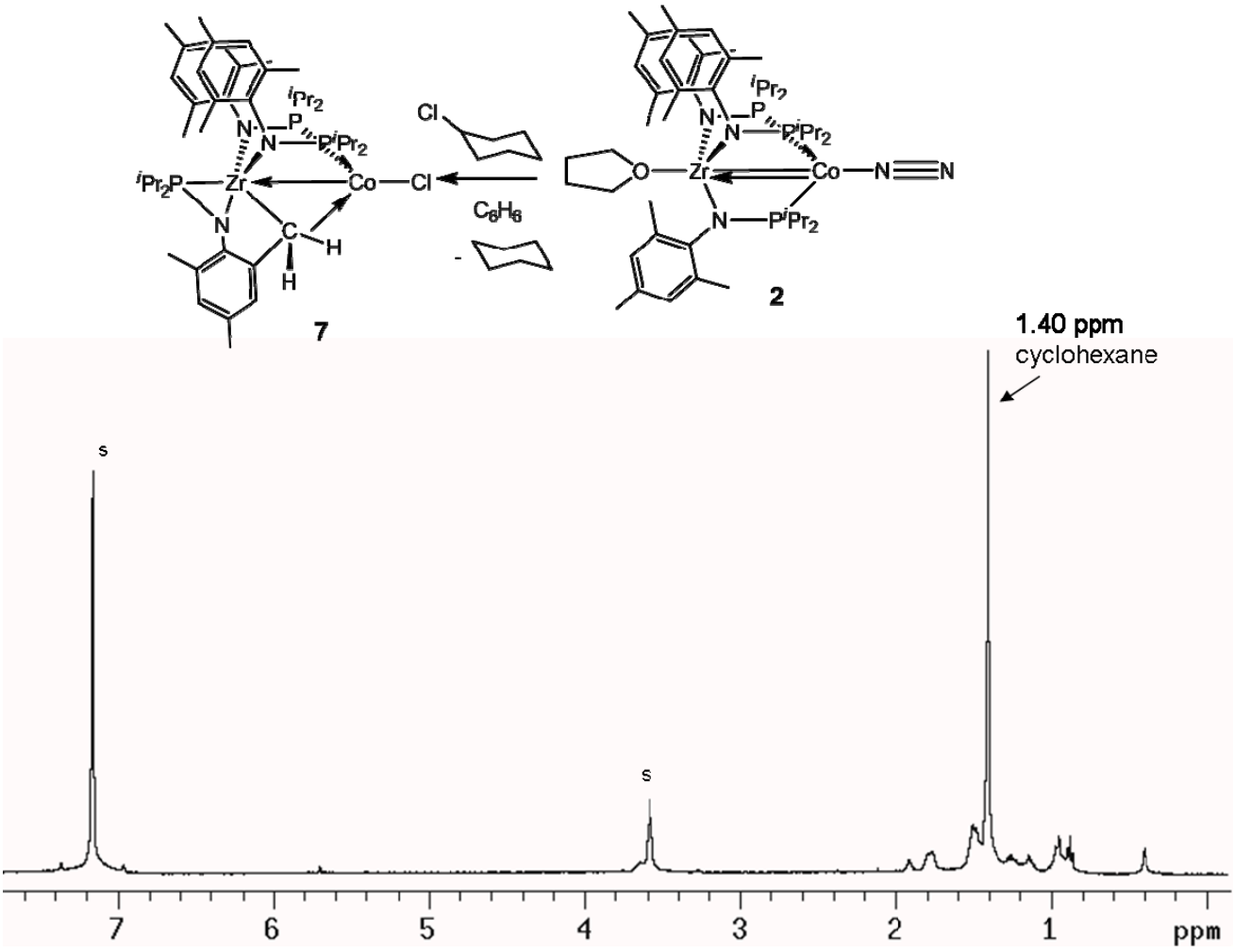


Figure S6. Comparison of ^{31}P and $^{31}P\{^{1}H\}$ NMR spectra and ^{1}H and $^{1}H\{^{31}P\}$ NMR spectra of **8**.

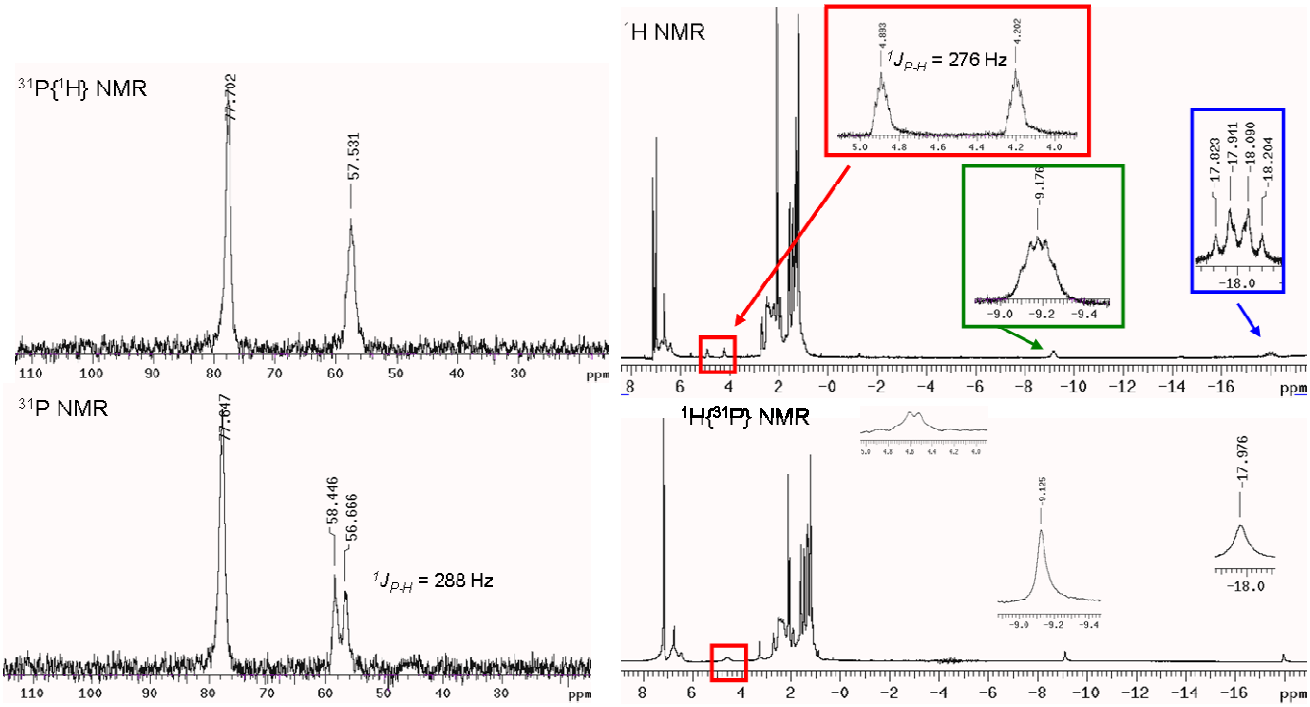


Figure S7. Variable temperature ^{31}P and ^{1}H NMR spectra of **8** in the 20 °C to -60 °C range.

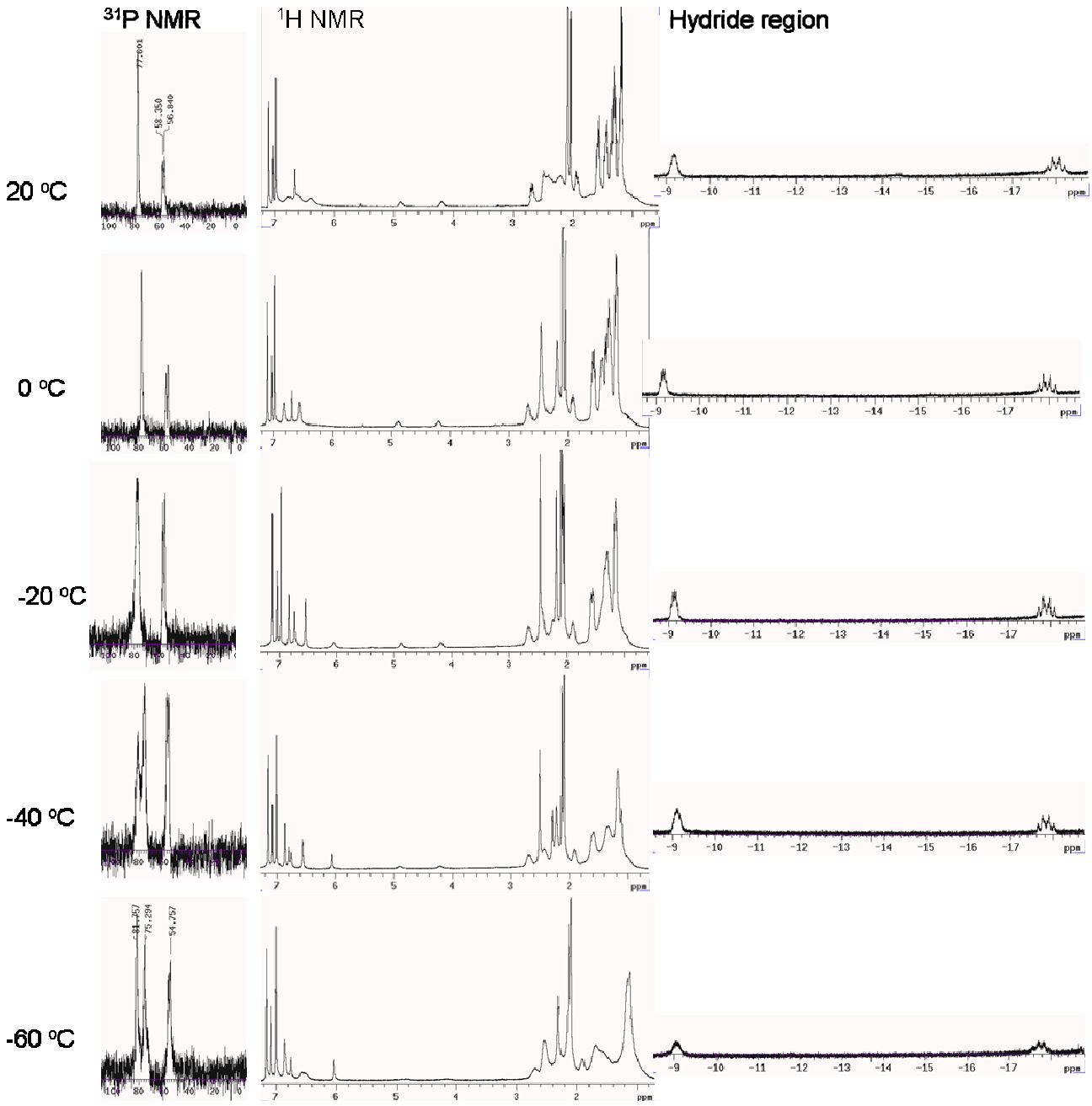
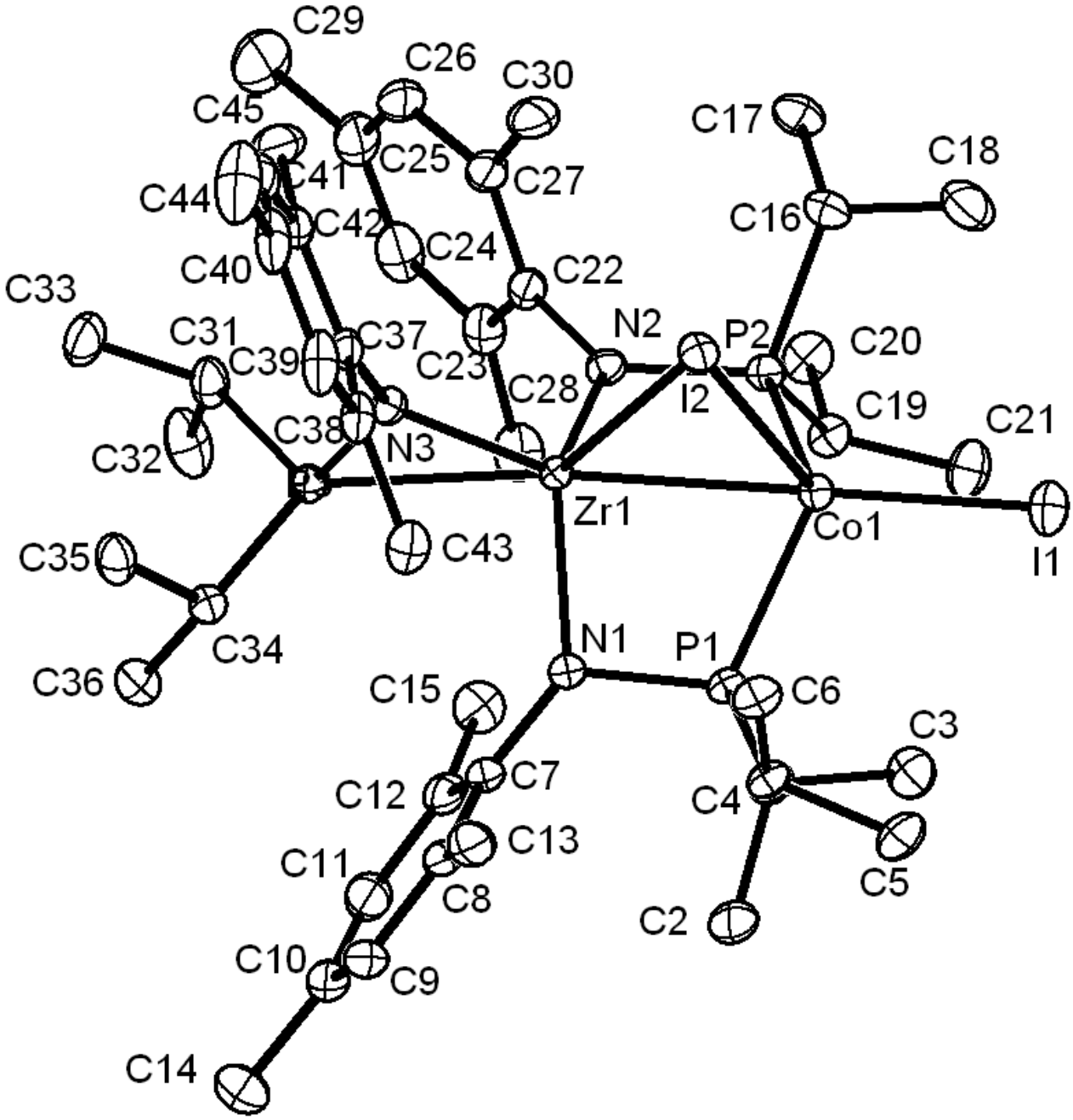


Figure S8. Fully-labeled ellipsoid representation of **4**.



X-Ray data collection, solution, and refinement for 4. Data collection carried out at 120 K, using a frame time of 10 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of seven phi and five omega scan sets, with 0.5° steps in phi or omega; completeness was 99.7%. A total of 4940 frames were collected. Final cell constants were obtained from the xyz centroids of 9918 reflections after integration.

From the systematic absences and the observed metric constants and intensity statistics, space group *C*2/*c* was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using the raw Patterson function and subsequent electron-density difference syntheses. Refinement (full-matrix-least squares) was carried out using the Oxford University *Crystals for Windows* program.[12] All ordered non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps (including H atoms attached to metal bound $-CH_3$ moieties), the H atoms were initially refined with soft restraints on the bond lengths and angles to regularise 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. During the structure solution, electron density difference maps revealed that there were considerable disordered solvent molecules (from history, likely *n*-pentane) in a volume of 2562.8 $Å^3$ per unit cell (22.3%); the peaks could not be modeled successfully. Areas of continuous electron density appeared in the *ac* plane (in the *n*-glide planes), creating bilayer arrangements at b = ¼ and ¾ as shown below.[13]

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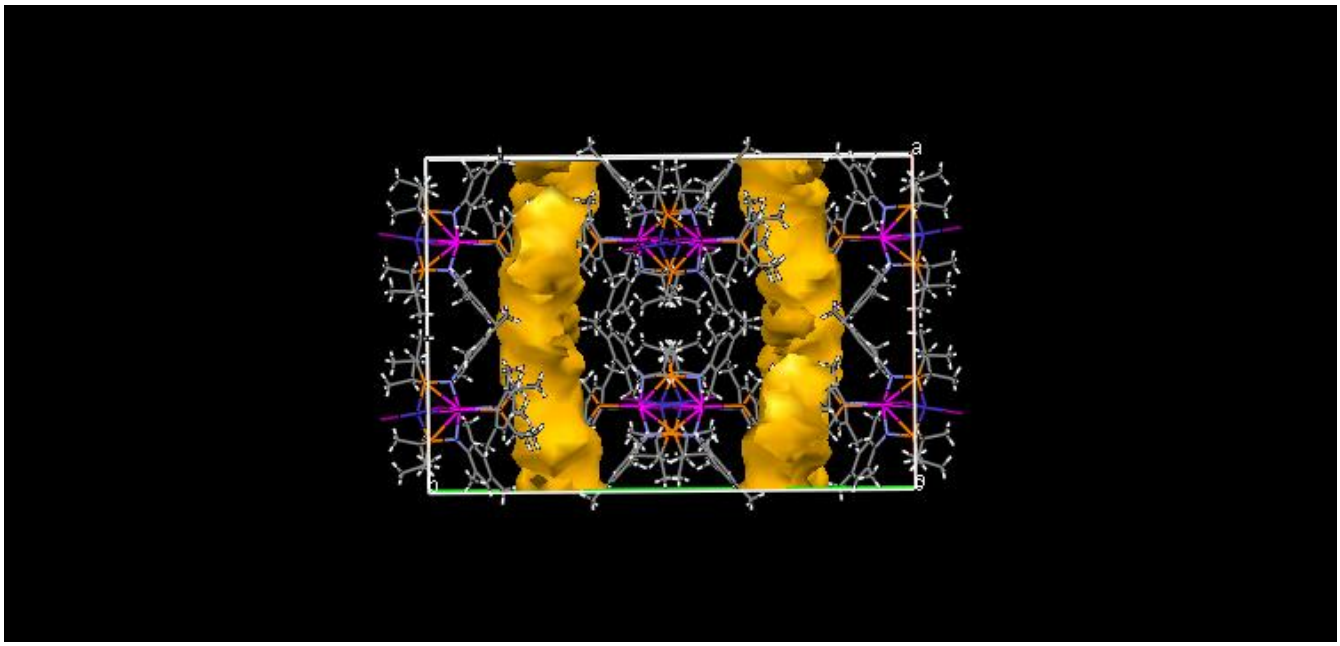
[12] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Cryst.* **2003**, *36*, 1487.

[13] Macrae, C. F; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Cryst.*, **2008**, *41*, 466-470.



Attempts at modeling the disordered *n*-pentane using restraints was unsuccessful, as was step by step acquisition of peaks using successive electron density difference maps. Thus, the structure factors were modified using the PLATON SQUEEZE[14,15] technique, in order to produce a "solvate-free" structure factor set. PLATON reported a total electron density of 536 e^- per unit cell, likely representing twelve *n*-pentane molecules. Use of the SQUEEZE technique resulted in a decrease of *ca* 1.6 % in *R*. The final least-squares refinement converged to $R_1 = 0.0228$ ($I > 2\sigma(I)$, 13736 data) and $wR_2 = 0.0608$ (F^2, 16791 data, 496 parameters). The final CIF is available as supporting material; we note that the the CheckCIF routine produced an alert G item, related to the void volume described above. Accordingly, the CIF file contains a section that explains these issues in detail. Two alert B errors involving the Hirshfeld test as well as an H atom Uiso ratio alert, are also explained in the CIF.

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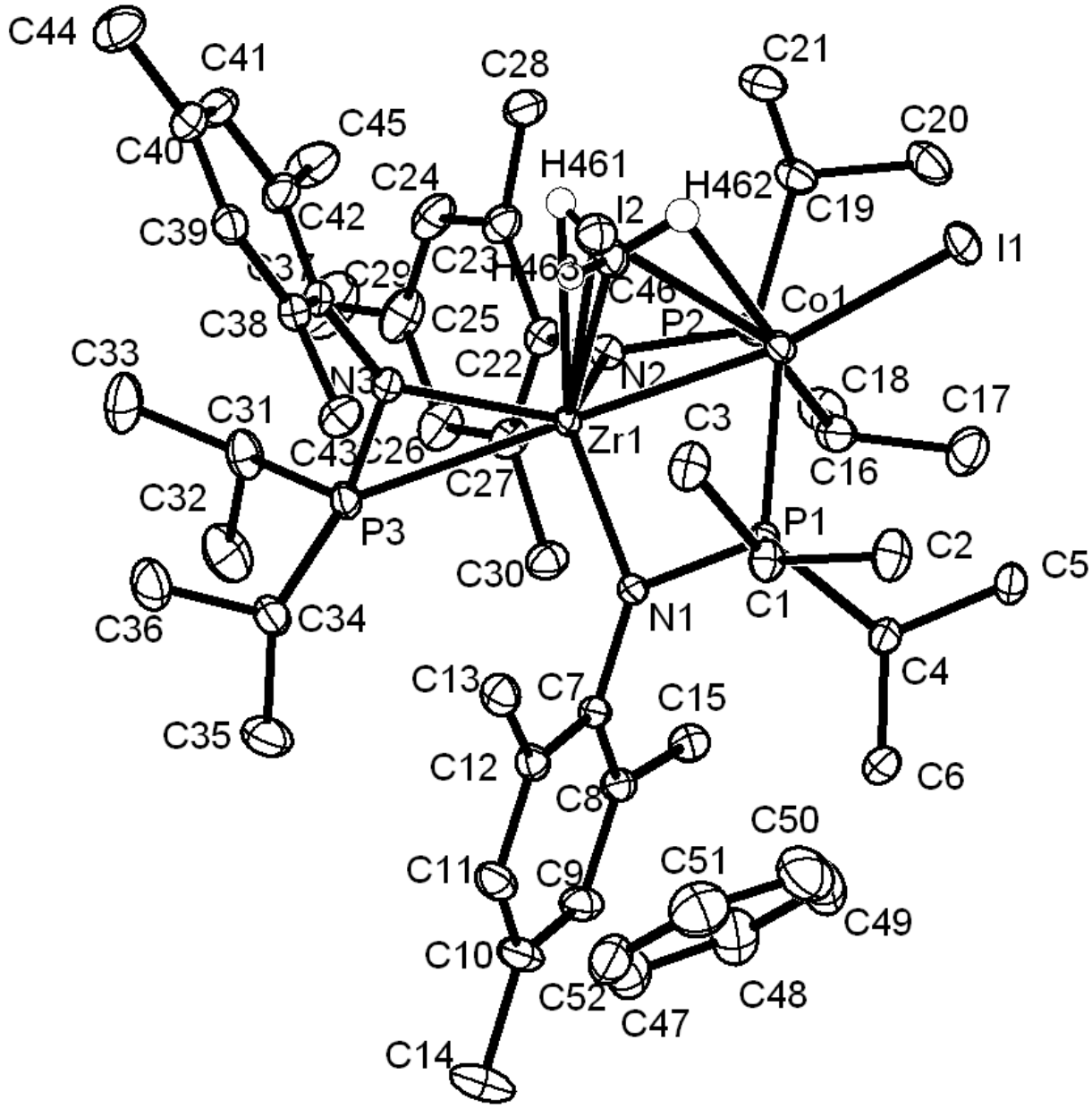
[14] v. d. Sluis, P.; Spek, A. Acta Crystallogr., Sect. A **1990**, A46, 194-201.

[15] (a) Spek, A. L. Acta Crystallogr., Sect A **1990**, A46, C34. (b) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, Spek, A. L. 1998.

Figure S9. Fully labeled ellipsoid representation of 5·C_6H_6.



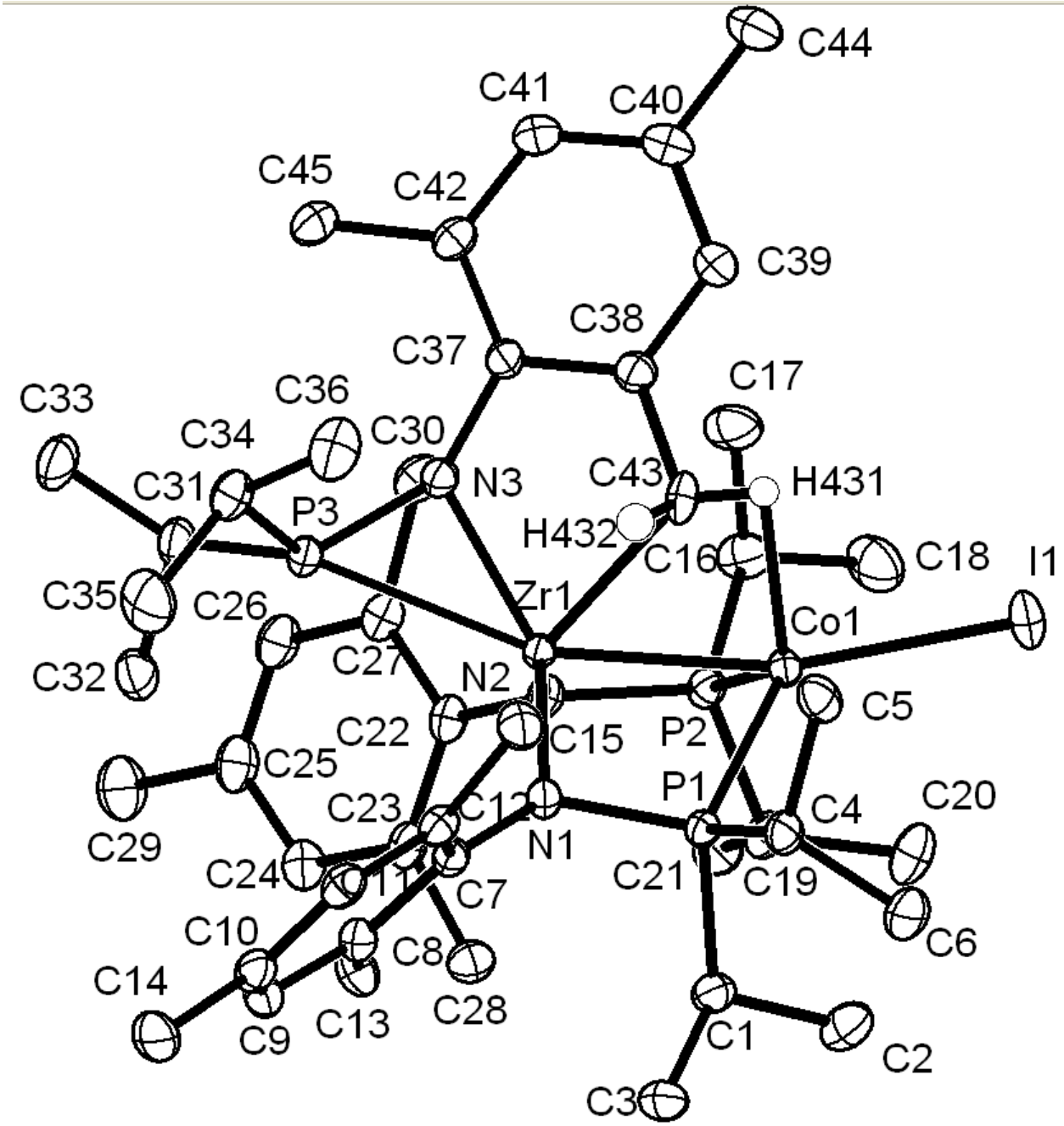
X-Ray data collection, solution, and refinement for 5. Data collection was carried out at 120 K, using a frame time of 10 sec and a detector distance of 60 mm. The optimized strategy used for data

collection consisted of seven phi and five omega scan sets, with 0.5° steps in phi or omega; completeness was 99.6%. A total of 4679 frames were collected. Final cell constants were obtained from the xyz centroids of 9314 reflections after integration.

From the systematic absences and 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 SuperFlip,[16] and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.[12] All ordered non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps (including H atoms attached to metal bound $-CH_3$ moieties), the H atoms were initially refined with soft restraints on the bond lengths and angles to regularise 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. Compound CMT_31 exhibited disorder of the bridging methyl group and a small amount of bridging iodide ion. The disorder was described with a constraint that the occupancies of the methyl group and iodide sum to 1.0. Carbon atom C(46) and its H atoms had an occupancy of 0.9693(7), while iodide I(2) had a corresponding occupancy of 0.0307(3). The final least-squares refinement converged to $R_1 = 0.0185$ ($I > 2\sigma(I)$, 15133 data) and $wR_2 = 0.0480$ (F^2, 15766 data, 567 parameters). The final CIF is available as supporting material.

Figure S10. Fully labeled ellipsoid representation of 6.

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

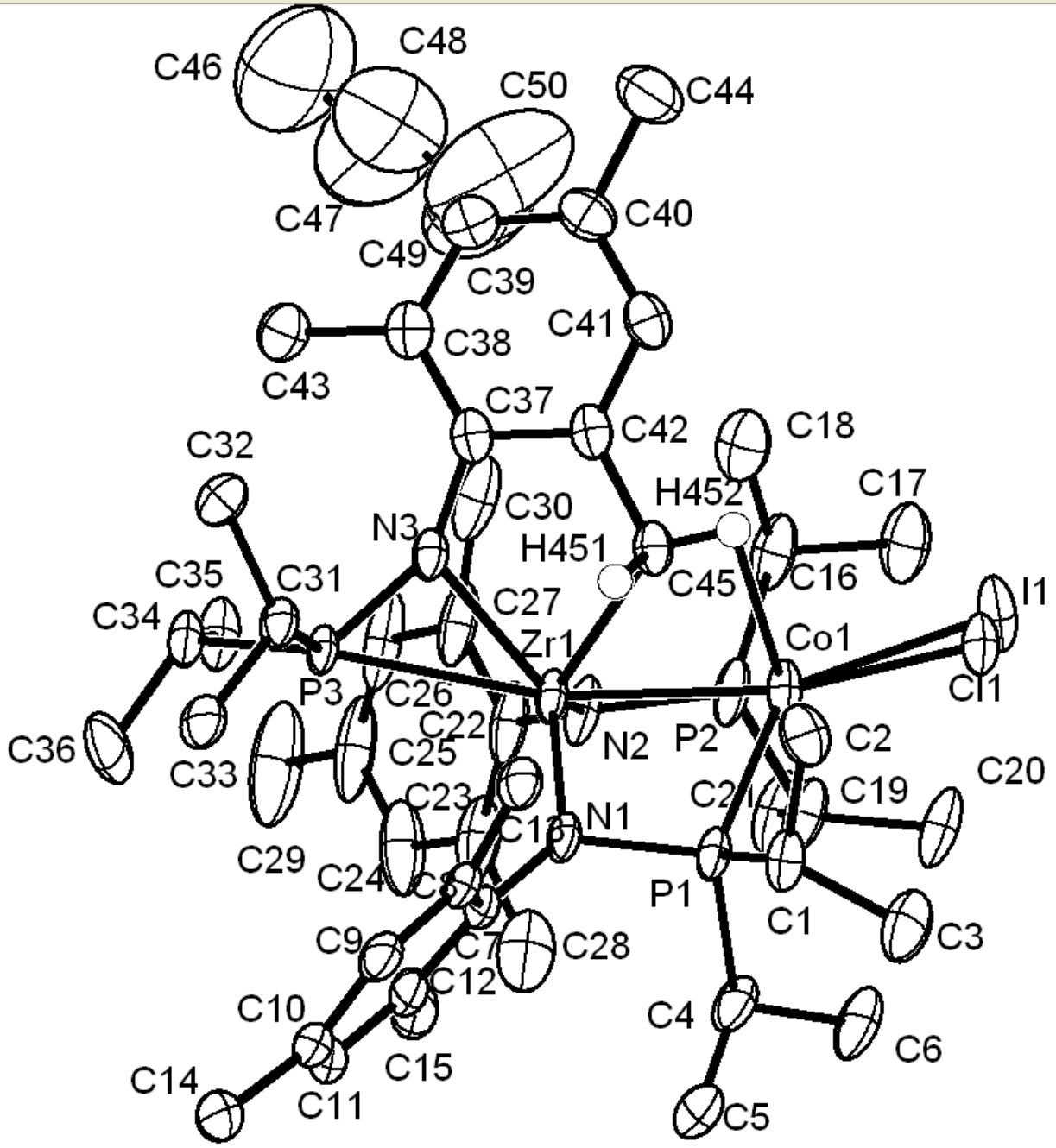

C44
C41
C40
C45
C42
C39
C38
C37
C17
C33
C36
C34
C30
C31
N3
C43
H431
P3
H432
C16
C18
I1
C35
C26
Zr1
Co1
C27
C32
N2
C5
C22
C15
P2
C25
P1
C23
C12
C4
C20
C29
N1
C24
C11
C7
C21
C19
C10
C8
C6
C14
C28
C9
C13
C1
C2
C3

X-Ray data collection, solution, and refinement for 6. Data collection was carried out at 120 K, using a frame time of 30 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of seven phi and two omega scan sets, with 0.5° steps in phi or omega; completeness was 99.6%. A total of 2132 frames were collected. Final cell constants were obtained from the xyz centroids of 9455 reflections after integration.

From the systematic absences and the observed metric constants and intensity statistics, space group $P2_1/n$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SIR92*,[17] and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.[12] 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 regularise 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 for all H atoms except H(431) and H(432) were refined with riding constraints. Atoms H(431) and H(432), attached to C(43), which symmetrically bridges the Zr-Co bond, were refined using distance and angle restraints (C-H, 0.95(5) Å; H-C-H and C-C-H, 109.5(10)º). The final least-squares refinement converged to $R_1 = 0.0322$ ($I > 2\sigma(I)$, 11309 data) and $wR_2 = 0.0859$ (F^2, 13879 data, 495 parameters). The final CIF is available as supporting material.

[17] Altomare, A; Cascarano, G; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst*. **1994**, *27*, 435.

Figure S11. Fully labeled ellipsoid representation of **7**·***n*-pentane.**



X-Ray data collection, solution, and refinement for 7·*n*-pentane. Data collection 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 four phi and four omega scan sets, with 0.5° steps in phi or omega; completeness was 99.0%. A total of 5460 frames were collected. Final cell constants were obtained from the xyz centroids of 9908 reflections after integration.

From the systematic absences and 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. Initial difficulty in solving the structure arose from an incorrect assignment of the unit cell; apparently arising from a misindexed twin. Reconsideration of the cell determination allowed choice of an appropriate unit cell, which was integrated assuming no twinning, and final refinement tests (TwinRotMat;[15] ROTAX[18]) indicated no contributions from a twin. The structure was solved using *SIR92* and subsequent electron-density difference syntheses.[17] Refinement (full-matrix-least squares) was carried out using the Oxford University *Crystals for Windows* program.[12] The structure exhibited disorder in the axial coordination to Co(1). It appeared that the complex was a mixture where either a Cl or I ion was bound to cobalt. Refinement of this model, with the occupancies of chloride and iodide constrained to sum to 1.0, gave 0.852(2) for the chloride occupancy; the Co-I distance was restrained to 2.57(1) Å. While the I/Cl disorder was modeled successfully, there were large peaks 1.5 - 2.0 e- near the Zr and Cl atoms, and several of the mesityl rings had large in-plane ellipsoid excursions, likely indicative of disorder. Attempts to model the other disorder (Zr, Co, mesityl) invariably failed, in part owing to the proximity of the atoms in question. 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 regularise 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

[18] Cooper, R. I.; Gould, R. O.; Parsons, S.; Watkin, D. J. *J. Appl. Cryst*. **2002,** *35*, 168-174

atom), after which the positions were refined with riding constraints. During the structure solution, electron density difference maps revealed that there were considerable disordered solvent molecules. One *n*-pentane molecule was located and successfully refined. From history, the remaining solvate was likely *n*-pentane or toluene in a volume of 588.8 $Å^3$ per unit cell (19.3%); the remaining peaks could not be modeled successfully. It appeared that the cavity area contained about two *n*-pentane molecules, located near the center of symmetry at (0, ½, 0) as shown in the *ac* projection below.[6] Modeling with or without restraints was unsuccessful, as was step by step acquisition of peaks using successive electron density difference maps. Thus, the structure factors were modified using the PLATON SQUEEZE[15,14] technique, in order to produce a "solvate-free" structure factor set (only for the *second* independent *n*-pentane molecule. PLATON reported a total electron density of 70 e^- per unit cell, likely representing two *n*-pentane molecules, consistent with our earlier observations. Use of the SQUEEZE technique resulted in a decrease of ca 1.3 % in *R*. The final least-squares refinement converged to $R_1 = 0.0669$ ($I > 2\sigma(I)$, 12534 data) and $wR_2 = 0.2032$ (F^2, 17679 data, 542 parameters). The final CIF is available as supporting material; we note that the CheckCIF routine produced an alert G item, related to the void volume described above, and one alert B item, related to the large range of hydrogen atom isotropic displacement parameters. Accordingly, the CIF file contains a validation reply form item and a section (_platon_squeeze_details) which explains these issues in detail.

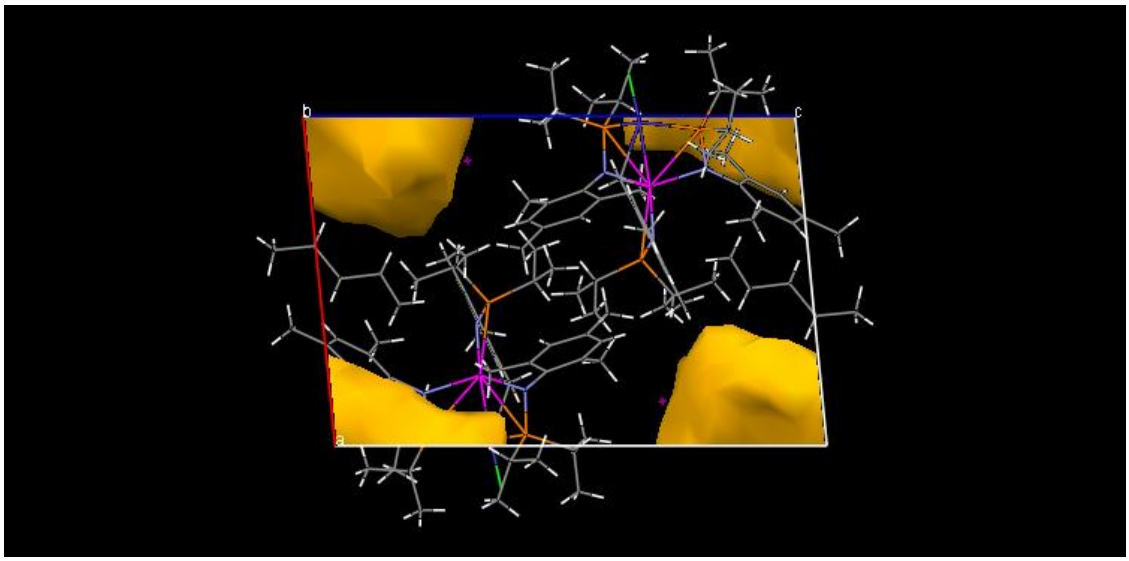
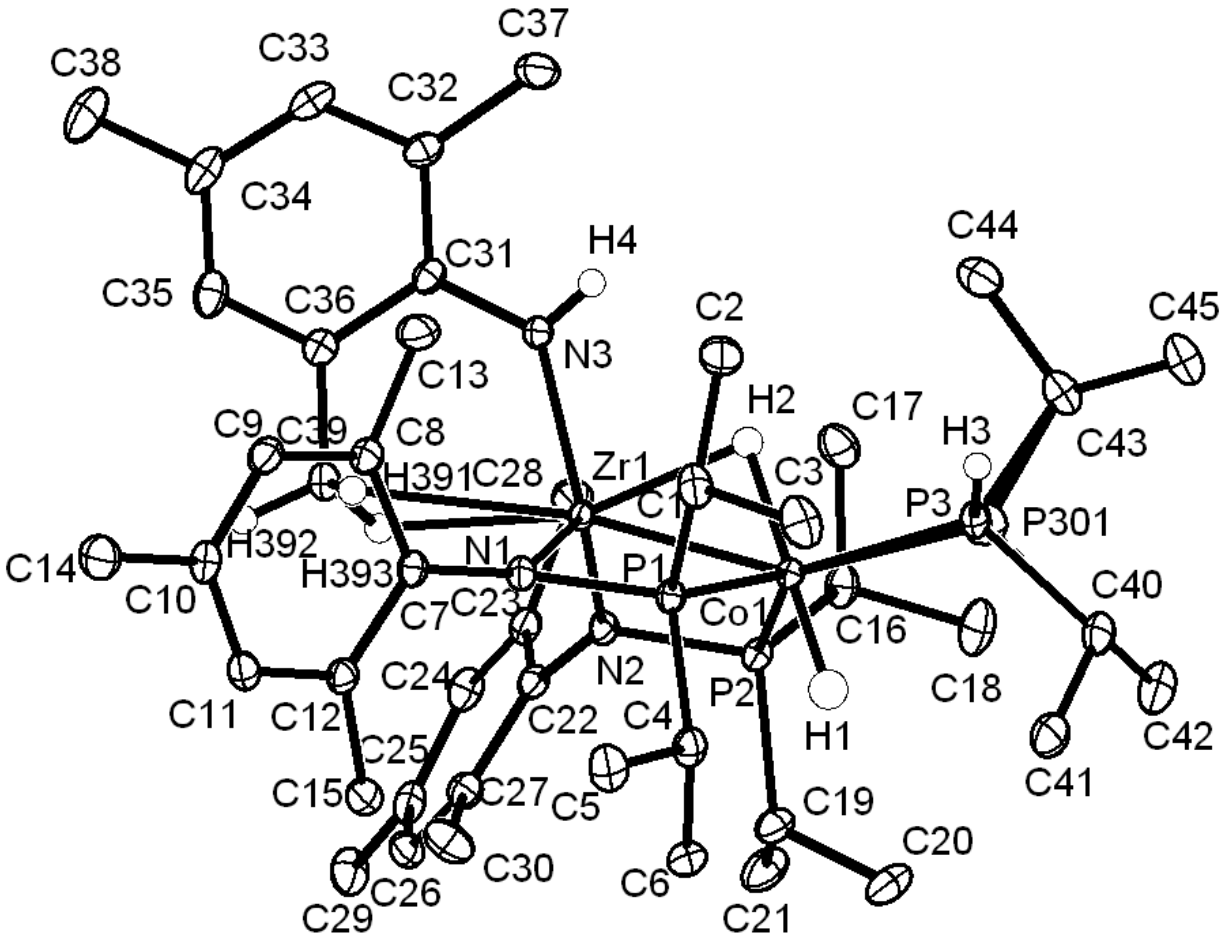


Figure S8. Fully labeled ellipsoid representation of **12.**



X-Ray data collection, solution, and refinement for 8. Data collection was carried out at 100 K, using a frame time of 25 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of four phi and six omega scan sets, with 0.5° steps in phi or omega; completeness was 99.7%. A total of 3759 frames were collected. Final cell constants were obtained from the xyz centroids of 9855 reflections after integration.

From the systematic absences and 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 early in the data collection using the raw Patterson function and successive difference Fourier syntheses,[12] and then refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.[12] All ordered non-hydrogen atoms were refined using anisotropic displacement parameters. After location of the H atoms attached to carbon on electron-density difference maps (including those on the agostic methyl C atom C(39), the H atoms were initially refined with soft restraints on the bond lengths and angles to regularise 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. An electron density difference map at this late point revealed the positions of the final four H atoms attached to N(3), P(3), Co(1) and bridging the Co-Zr bond. The data were of very high quality, with an overdetermination ratio of *ca.* 27; thus we tested the possible refinement of the latter four H atoms (H(1) through H(4)). Refinement proceeded smoothly and converged rapidly, yielding X-H distances with standard deviations in the vicinity of 0.02 Å. Inspection of the subsequent electron density difference map revealed a minor disorder of the diisopropylphosphine ligand. The disorder was small, and it was not possible to locate alternative sites for the C atoms. Thus, the sum of occupancies of the two P atoms involved in the disorder (P(3), P(301)) were constrained to sum to 1.0; the value of the occupancy for the major P atom, P(3), was 0.958(6). Atom P(301) was refined using an isotropic displacement parameter; disorder of the associated H atom was ignored. The final least-squares refinement converged to $R_1 = 0.0272$ ($I > 2\sigma(I)$,

10842 data) and wR_2 = 0.0665 (F^2, 13778 data, 499 parameters). The final CIF is available as supporting material.