Supporting information for:

Unusual activation of H_2 by reduced cobalt complexes supported by a PNP pincer ligand

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A1) Experimental section.

General considerations. Unless otherwise noted, all reactions were performed using standard Schlenk techniques under a N_2-atmosphere or in a N_2-atmosphere glove box. Solvents were dried by passing through a column of activated alumina and degassed with nitrogen.[1] C_6D_6 and $C_6D_5CD_3$ were dried over Na/benzophenone and vacuum transferred. All NMR spectra were obtained in C_6D_6 or $C_6D_5CD_3$ using Bruker AVQ-400, DRX-500 or AV-600 spectrometers. ^1H NMR chemical shifts (δ) were calibrated relative to the residual solvent peak. Magnetic susceptibility measurements were performed in C_6D_6 according to the Evans NMR method.[2] Melting points were determined using sealed capillaries prepared under a nitrogen atmosphere. Infrared (IR) spectra were recorded with a Thermo Scientific Nicolet iS10 series FTIR spectrophotometer as a powder or a Nujol mull between KBr plates. T_1 experiments were performed at 294 K, 253 K, 233 K, 213 K and at 193 K in $C_6D_5CD_3$ using a Bruker DRX-500 spectrometer. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility. X-ray crystal diffraction analyses were performed at the University of California, Berkeley CHEXRAY facility. [(HPNP)CoCl] (**1**), [(DPNP)CoCl] (**1-D**), $[(PNP)Co]_2$ (**3**) and [(PNP)CoCl] (**6**) were prepared according to literature procedures.[3] The remaining starting materials were obtained from Aldrich and used without further purification.

[(HPNP)CoCl(H)$_2$] (2). A J. Young NMR tube was filled with 0.5 mL of a $C_6D_5CD_3$ solution of **3** (11 mg, 0.03 mmol). The solution was freeze-pump evacuated three times and filled with an atmosphere of hydrogen. The reaction turned from blue to green. Crystals suitable for an X-ray diffraction study were grown from a concentrated solution of **3** in toluene cooled to -40ºC under hydrogen atmosphere, to give yellow, block-like crystals. A crystal was immediately transferred to the diffractometer and cooled by a nitrogen flow at 100 K. ^1H NMR ($C_6D_5CD_3$, 20 ˚C, 600

MHz): δ 2.71 (br, 5H, NCH_2 (4) + N*H* (1)), 1.92 (br, 2H, PC*H*$(CH_3)_2$), 1.83 (br, 2H, PC*H*$(CH_3)_2$), 1.68 (br, 2H, PCH_2), 1.57 (br, 2H, PCH_2), 1.44 (br, 6H, CH_3), 1.25 (br, 6H, CH_3), 1.03 (br, 6H, CH_3), 0.77 (br, 6H, CH_3), -23.60 (q, at -80˚C: -23.54, td, 1H, CoH, $J_{\text{H-P}}$: 55 Hz, $J_{\text{H-H}}$: 42 Hz), -30.02 (q, at -80˚C: -30.03, td, 1H, CoH, $J_{\text{H-P}}$: 51 Hz, $J_{\text{H-H}}$: 42 Hz). ^{31}P {^{1}H} NMR: ($C_6D_5CD_3$, 20 ˚C, 162 MHz) δ 52.4 (br). ^{13}C {^{1}H} NMR: ($C_6D_5CD_3$, 20 ˚C, 150.9 MHz) δ 55.5 (m, N*C*), 32.7 (t, P*C*H), 26.2 (t, P*C*H_2), 23.2 (t, P*C*H_2), 21.9 (t, P*C*H), 21.8 (s, *C*H_3), 19.6 (s, *C*H_3), 18.2 (s, *C*H_3).

[(HPNP)CoCl(D)$_2$] (2-D$_2$) and **[(HPNP)CoCl(H)D] (2-HD).** The reactions were carried out in an analogous manner to that of **2** with D_2 or HD respectively. **2-D$_2$**: ^{2}H NMR ($C_6D_5CD_3$, 20˚C, 92.12 MHz): δ -23.55 (t, Co-H, $J_{\text{D-P}}$: 8 Hz), -30.08 (t, Co-H, $J_{\text{D-P}}$: 8 Hz). **2-HD**: ^{1}H NMR ($C_6D_5CD_3$, 20˚C, 600 MHz): δ 2.77 (br, 3H, NCH_2 (2) + N*H* (1)), 2.65 (br, 2H, NCH_2), 1.93 (br, 2H, PC*H*$(CH_3)_2$), 1.80 (br, 2H, PC*H*$(CH_3)_2$), 1.66 (br, 2H, PCH_2), 1.53 (br, 2H, PCH_2), 1.46 (br, 6H, CH_3), 1.21 (br, 6H, CH_3), 1.02 (br, 6H, CH_3), 0.78 (br, 6H, CH_3), -23.45 (t, at -60˚C: -23.39, t, 1H, Co-H, $J_{\text{H-P}}$: 56 Hz), -29.92 (br, at -60˚C: -29.95, t, 1H, Co-H, $J_{\text{H-P}}$: 49 Hz). ^{1}H {^{31}P} NMR ($C_6D_5CD_3$, -60˚C, 600 MHz) δ -23.39 (s), -23.48 (s, assigned to **2**), -29.95 (s), -30.04 (s, assigned to **2**). $J_{\text{H-D}}$ = 6 Hz (at -80˚C).

[(PNP)CoH]$_2$ (4). A Schlenk tube was filled with a solution of [(PNP)Co]$_2$ (**3**) (0.15 g, 0.21 mmol) in 15 mL of toluene at room temperature. The solution was evacuated and filled with an atmosphere of hydrogen. The reaction mixture was stirred for 48 h, resulting in a color change from brown to brown-yellow. The solvent was removed under vacuum, and the product was extracted with hexane (3 x 10 mL). The solution was concentrated and cooled to -40°C to give brown, block-like, crystals (0.08 g, 53 %). Crystals suitable for an X-ray diffraction study were grown from a concentrated solution of diethyl ether cooled to -40ºC. ^{1}H NMR ($C_6D_5CD_3$, 20˚C, 400 MHz): δ 4.85 (br), 3.72 (br), 3.27 (br), 3.10 (br), 2.77 (br), 2.42 (br), 2.24 (br), 1.90 (br), 1.65 (br), 1.54 (br), 1.34 (br), 1.20 (br), 1.12 (br), 1.07 (br), 0.89 (br), 0.44 (br), -22.04 (dt, at -80˚C: ddd, Co-H, ${}^{2}J_{H\text{-}P}$: 87 Hz for *trans* P; ${}^{2}J_{H\text{-}P}$: 22 Hz for *cis* P; ${}^{3}J_{H\text{-}P}$: 18 Hz). ${}^{31}P$ {${}^{1}H$} NMR: (C_6D_6, 20 ˚C, 162 MHz) δ 78.02 (br), 54.92 (br). IR (cm^{-1}) 1883 (s, Co-H), 1361 (m), 1260 (m), 1236 (w), 1026 (s), 880 (m), 812 (m), 640 (w), 607 (w). Anal. Calc: C, 52.74; H, 10.24; N, 3.84. Observed C, 52.74; H, 10.21; N, 3.87. Mp 159-161°C (dec.). $\mu_{eff} = 0.7\ \mu_B$/Co.

[(PNP)CoD]$_2$ (4-D$_2$). The synthesis was carried out analogously to that of **4** under a D_2 atmosphere, starting with **3** (0.50 g, 0.69 mmol), to yield brown, block-like crystals (0.15 g, 30 %) after crystallization from hexane. ${}^{2}H$ NMR ($C_6D_5CD_3$, 20˚C, 92.12 MHz): δ -21.88 (d, Co-D). ${}^{31}P$ {${}^{1}H$} NMR ($C_6D_5CD_3$, 20 ˚C, 162 MHz): δ 78.34 (br), 55.38 (br). IR (cm^{-1}) 2803 (s), 1548 (s, D-Co), 1356 (s) 1261 (m), 1235 (m), 1179 (w), 1151 (m), 1026 (s), 881 (s), 811 (m), 700 (w), 666 (w), 641 (m), 606 (m).

[(PNP)CoCO] (5). Carbon monoxide (16.5 mL, 0.68 mmol) was added via syringe into a solution of **4** (0.25 g, 0.34 mmol) in 15 mL of hexane at room temperature. The reaction mixture was stirred overnight and no color change was observed. The solution was concentrated and cooled to -40 °C to give brown, block-like, crystals (0.14 g, 53 %). Crystals suitable for an X-ray diffraction study were grown from a concentrated solution of hexane cooled to -40ºC. ${}^{1}H$ NMR (C_6D_6, 20˚C, 400 MHz): δ 3.33 (m, 4H, NC*H$_2$*), 2.18 (m, 4H, PC*H*(CH$_3$)), 1.89 (m, 4H, PC*H$_2$*), 1.39 (m, 12H, C*H$_3$*), 1.16 (m, 12H, C*H$_3$*). ${}^{31}P$ {${}^{1}H$} NMR (C_6D_6, 20 ˚C, 162 MHz): δ 102.52 (s). ${}^{13}C$ {${}^{1}H$} NMR (C_6D_6, 20 ˚C, 100.6 MHz) 60.5 (m, N*C*H$_2$), 25.4 (t, P*C*H(CH$_3$)), 24.4 (t, P*C*H$_2$), 19.1 (s, *C*H$_3$), 17.7 (s, *C*H$_3$). IR (cm^{-1}) 2815 (m), 2782 (s), 1882 (s, C-O), 1104 (s), 1023 (s), 882 (s), 814 (s), 718 (s), 657 (s), 633 (s). Anal. Calc: C, 52.17; H, 9.27; N, 3.58. Observed C, 52.31; H, 9.14; N, 3.60. Mp 154-156°C.

[(HPNP)Co(H)$_3$] (7). A solution of (PNP)CoCl (**6**) (0.30 g, 0.75 mmol) in 10 mL of diethyl ether was added to a suspension of KC_8 (0.13 g, 0.96 mmol) in 10 mL of diethyl ether at -78 °C under a hydrogen atmosphere (1 atm). The reaction mixture was allowed to warm to room temperature and was stirred for 16 h. Graphite was formed and no color change was observed. The solvent was removed under vacuum, and the product was extracted with hexane (3 x 10 mL) keeping the H_2 atmosphere. The solution was concentrated and cooled to -40 °C to give brown, block-like crystals (0.08 g, 29 %). Crystals suitable for an X-ray diffraction study were grown from a concentrated solution of diethyl ether cooled to -40ºC under a hydrogen atmosphere. ^{1}H NMR ($C_6D_5CD_3$, 20˚C, 500 MHz): δ 19.52 (br), 12.13 (br), 4.77 (br), 3.97-0.10 (multiple resonances, not assigned), -9.01 (br), -12.49 (br, at -40˚C: two td (-12.29, -12.55), 2H, Co-H$_{trans}$, $J_{\text{H-H}}$: 19 Hz, $J_{\text{P-H}}$: 46 Hz), -13.51 (br), -26.25 (br, at -40˚C: tt, 1H, Co-H$_{cis}$, $J_{\text{H-H}}$: 19 Hz, $J_{\text{H-P}}$: 60 Hz). ^{31}P {^{1}H} NMR ($C_6D_5CD_3$, 20˚C, 162 MHz): δ 111.9 (br), 55.1 (br), -1.2 (s), -2.1 (s). IR (cm^{-1}) 1880 (w), 1839 (w), 1816 (w), 1548 (m), 1364 (s), 1261 (w), 1239 (m), 1152 (s), 1097 (m), 1025 (s), 883 (s), 821 (m). Anal. Calc: C, 52.31; H, 10.97; N, 3.81. Observed C, 51.01; H, 10.81; N, 3.59. Despite several attempts, low C values were obtained. Mp 118-120°C.

[(DPNP)Co(D)$_3$] (7-D$_2$) and **[((D/H)PNP)Co(D/H)$_3$] (7-HD).** A solution of **6** (0.050 g, 0.12 mmol) in 5 mL of THF was added to a suspension of KC_8 (0.022 g, 0.16 mmol) in 5 mL of THF at -78°C under Ar atmosphere. The Schlenk was evacuated and then filled with 1 atmosphere D_2 or HD respectively. The reaction mixture was allowed to warm to room temperature and was stirred for 16 h. Graphite was formed and no color change was observed. The solvent was removed under vacuum, and the product was extracted with $C_6D_5CD_3$ in the glove box, filtered and placed in a J. Young NMR tube. ^{2}H NMR ($C_6D_5CD_3$, 20˚C, 600 MHz): δ -13.64 (br), -15.58

(br), -17.70 (br), -20.40 (br), -24.25 (br). **7-HD:** $^1H\ \{^{31}P\}$ NMR ($C_6D_5CD_3$, -60˚C, 600 MHz): δ -12.20 (br), -12.38 (br), -12.58 (br), -25.61 (br), -25.83 (br), -26.18 (br).

Equilibrium constant measurements by UV-Vis. ***1/2 equilibrium*****:** A 0.007 M solution of **1** in toluene was prepared in the glove-box and placed in a 1 cm Schlenk-type quartz cell. The absorbance at 605 nm was measured from -40˚C to 80˚C using Varian Cory 50 UV-Vis spectrophotometer, and fitted to a line by the least square method to obtain the ε value as a function of temperature (toluene density values were obtained from the literature).[4, 5] The solution was then frozen in liquid nitrogen, evacuated and refilled with an atmosphere of H_2 in a Schlenk line (the procedure was repeated 3 times). The absorbance was measured at 605 nm to follow the concentration of **1** in the 10˚C - 80˚C temperature range. Values were recorded each 10˚C, waiting at least 5 min once the target temperature was reached to ensure equilibrium. A 1 atm H_2 pressure was kept during the experiment and the H_2 concentration in toluene was obtained from literature values.[5, 6] The equilibrium constant was calculated by the formula K = [**2**]/([**1**][H_2]) (where [H_2] = conc. H_2 in toluene at 1 atm. and [**2**] = 0.007-[**1**]), using the ε values previously obtained. A Van't Hoff plot was generated with the data and fitted to a line by the least-square method.

Crystallographic Analyses. Single crystals of **2**, **4**, **5** and **7** were coated in Paratone-N oil, mounted on a Kaptan loop, transferred to a Bruker SMART APEX or APEX II QUAZAR diffractometer with CCD area detector,[7] centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that has been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrixes and cell constants were determined by collection of 60 10-s frames, followed by spot integration and least-squares refinement. A data collection strategy was computed with COSMO to ensure a redundant and complete data set, and the raw data were integrated using SAINT.[8] The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.[9] XPREP[10] was used to determine the space group. The structures were solved using SHELXS[11] and refined on all data by full-matrix least-squares with SHELXL-97.[12] Thermal parameters for all non-hydrogen atoms were refined anisotropically. ORTEP diagrams were created using ORTEP-32.[13]

Computational Details. All structures and energies were calculated using the Gaussian09 suite of programs.[14] Self-consistent field computations were performed with tight convergence criteria on ultrafine grids, while geometry optimizations were converged to tight geometric convergence criteria for all compounds. Spin expectation values <S>2 indicated that spin contamination was not significant in any case. Frequencies were calculated analytically at 298.15 K and 1 atmosphere. Structures were considered true minima if they did not exhibit imaginary vibration modes. Optimized geometries were compared using the sum of their electronic and zero-point energies. In order to reduce the computational time, the isopropyl groups attached to phosphorous were substituted for methyl groups. The TPSS and B3LYP functionals were used throughout this computational study. For geometry optimizations and frequency calculations all atoms were treated with 6-31++G(d,p) basis set with TPSS functional and with 6-311++G(d,p) basis set for the B3LYP functional.[14] A 5d diffusional function was used for all atoms except H, and no polarization functions were added for H.

B1) ^{1}H NMR spectrum for [(HPNP)CoCl] (**1**)

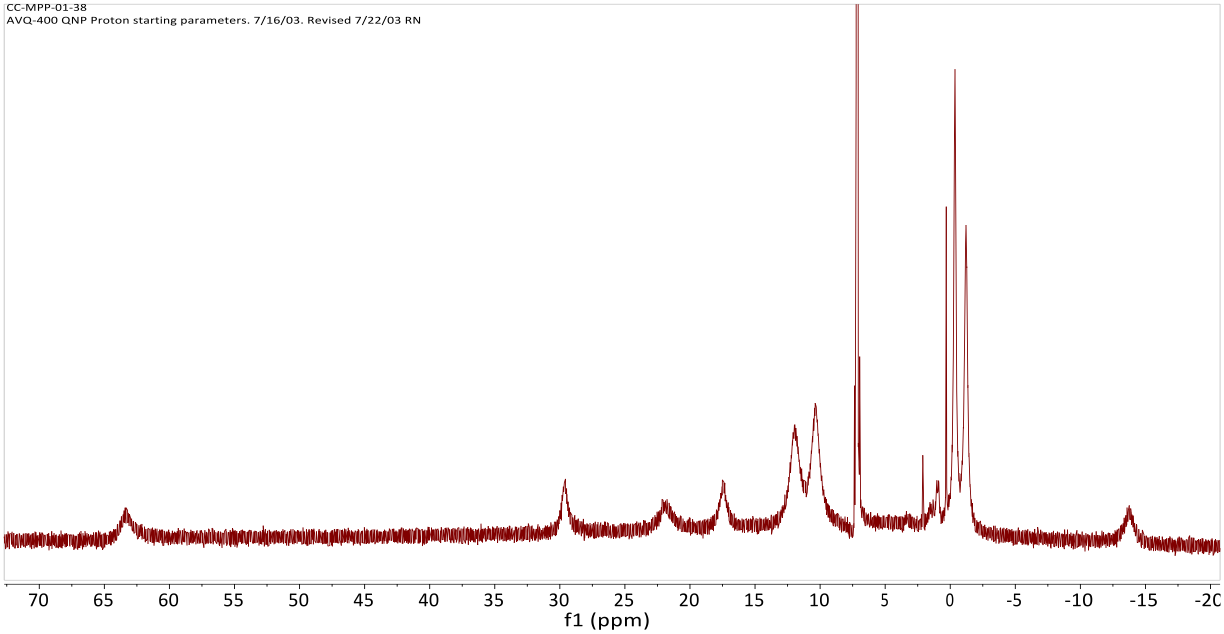

Figure 1. ^{1}H NMR spectrum (C_6D_6, 20°C, 400 MHz) for [(HPNP)CoCl] (**1**).

B2) ^{1}H NMR spectra for [(HPNP)CoCl(H)$_2$] (**2**).

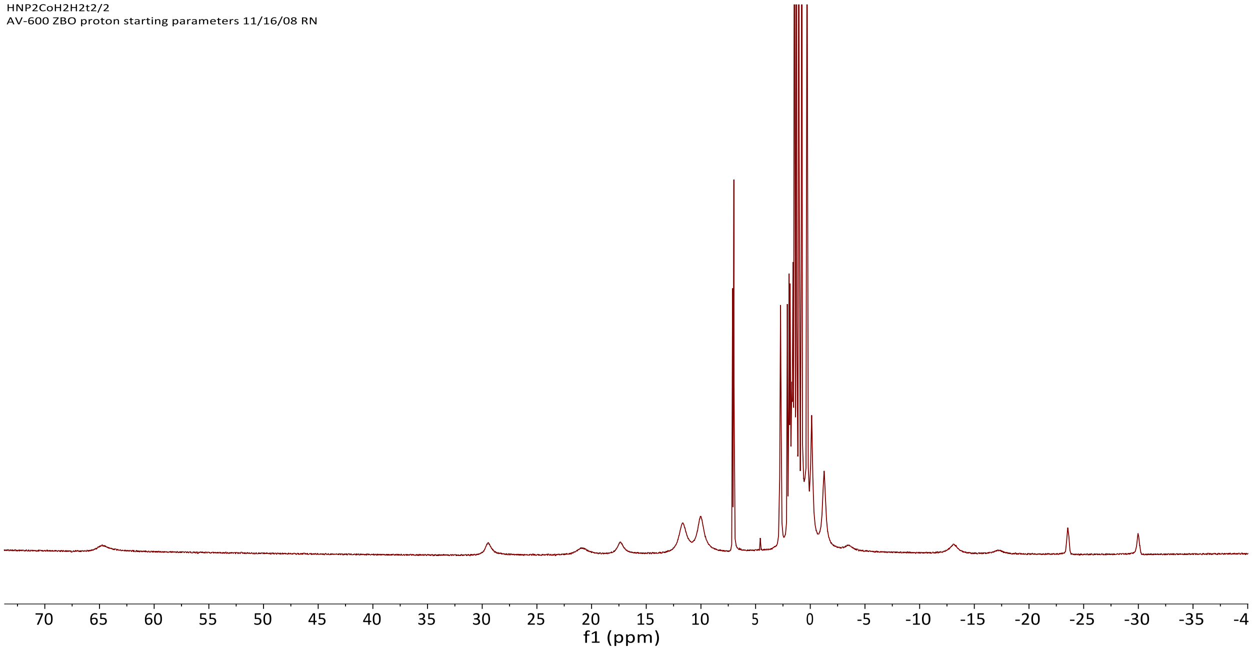

Figure 2. ^{1}H NMR spectrum ($C_6D_5CD_3$, 20°C, 600 MHz) for the reaction of **1** with H_2. The resonances for both **1** and [(HPNP)CoCl(H)$_2$] (**2**) are observed as these species are in equilibrium under a H_2 atmosphere.

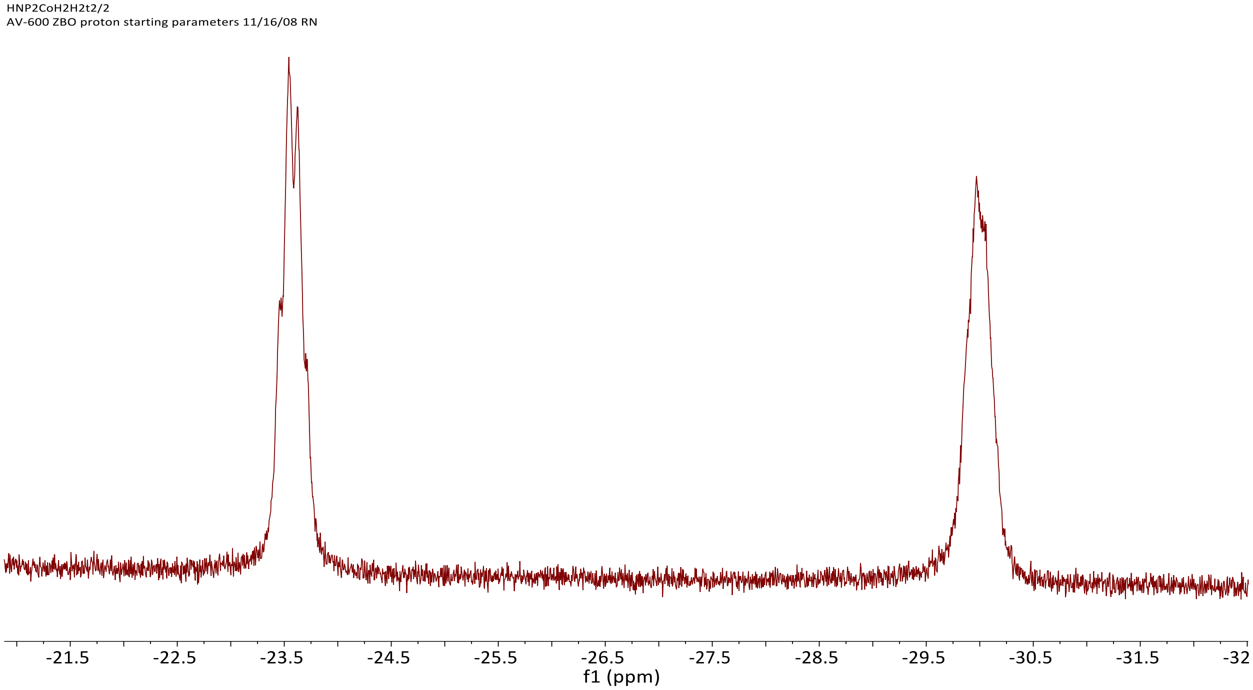

Figure 3. ^{1}H NMR spectrum ($C_6D_5CD_3$, 20°C, 600 MHz) for the reaction of **1** with H_2. The resonances observed at -23.60 and -30.02 ppm are assigned to the two hydride ligands (*cis* and *trans* to nitrogen respectively) in **2**.

B3) ^{2}H NMR for [(HPNP)CoCl(D)$_2$] (**2-D$_2$**)

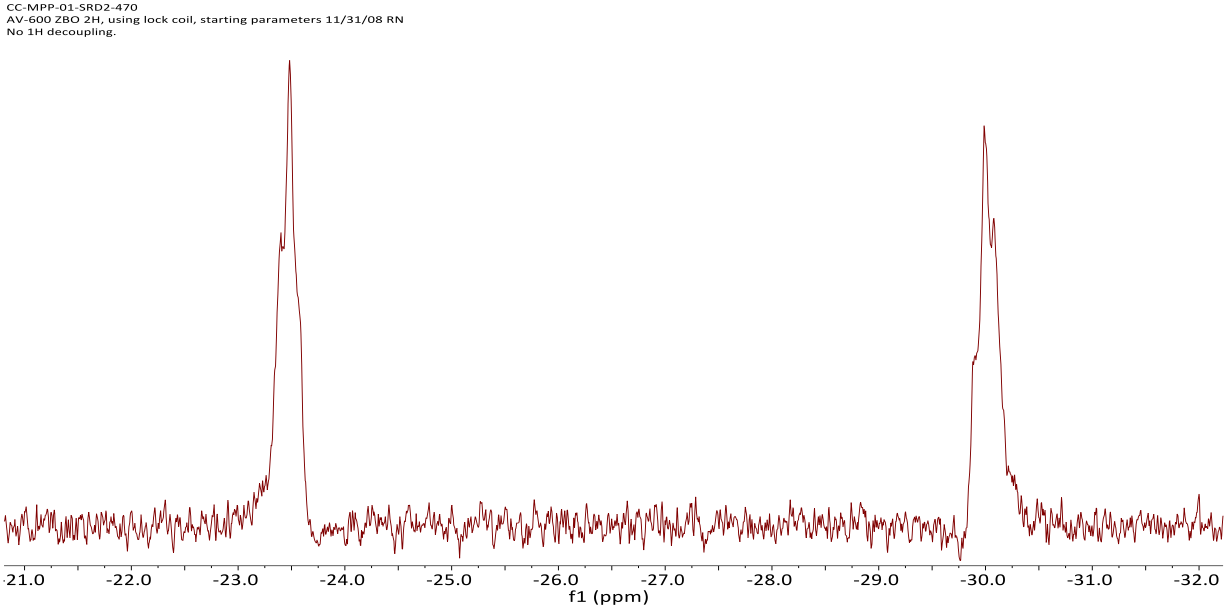

Figure 4. ^{2}H NMR spectrum ($C_6D_5CD_3$, 20°C, 92.12 MHz) for the deuteride resonances in [(HPNP)CoCl(D)$_2$] (**2-D$_2$**).

B4) $^{1}H\ \{^{31}P\}$ NMR spectra for [(HPNP)CoCl(H)D] (**2-HD**)

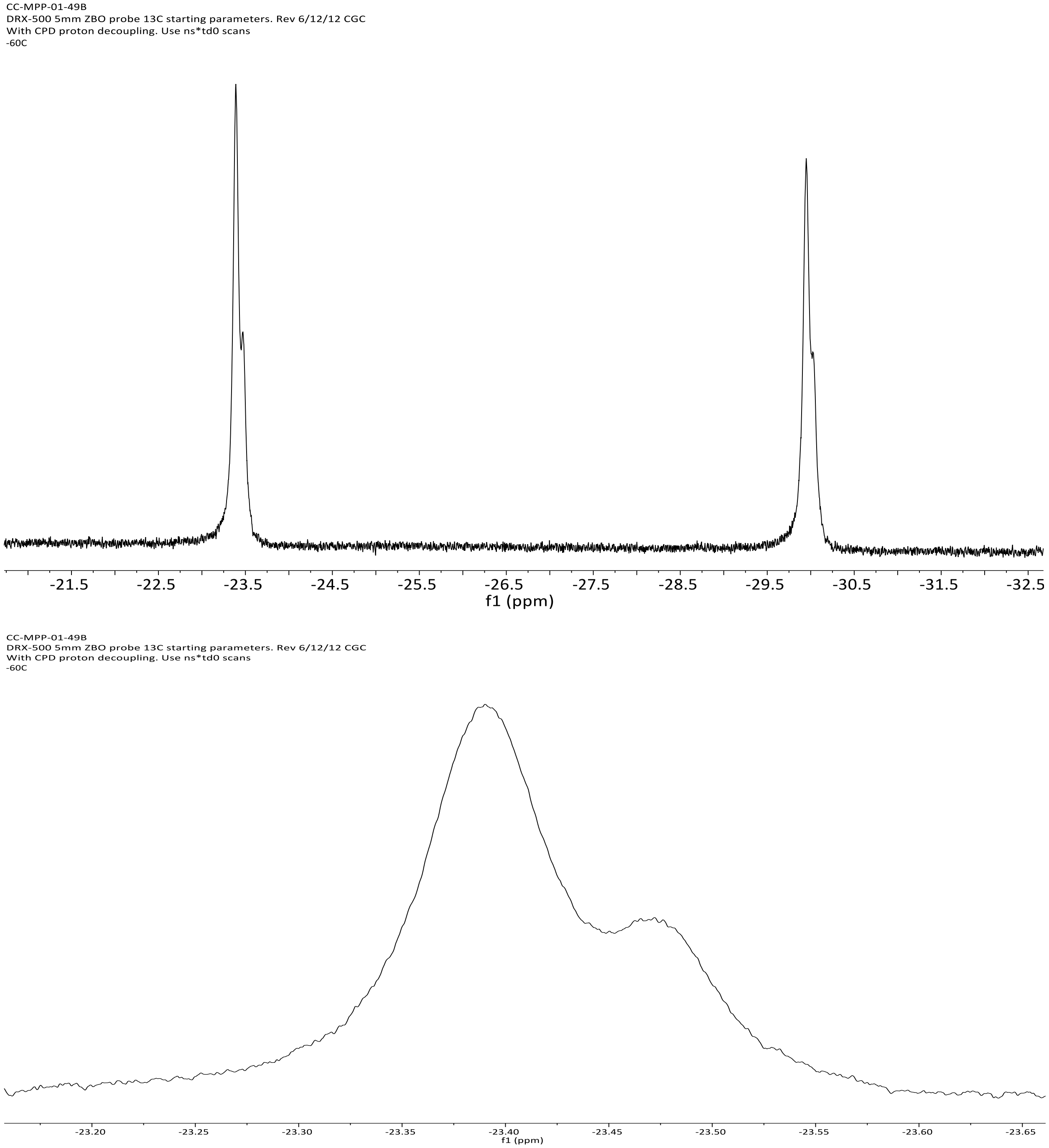

Figure 5. Top: $^{1}H\ \{^{31}P\}$ NMR spectrum ($C_6D_5CD_3$, -60˚C, 500 MHz) for the hydride resonances in [(HPNP)CoCl(HD)] (**2-HD**). Bottom: enlarged *cis* to nitrogen hydride resonance ($C_6D_5CD_3$, -60˚C, 500 MHz) showing the species assigned as [(HPNP)CoCl(H)D] (**2-HD**,-23.39 ppm) and [(HPNP)CoCl(H)$_2$] (**2**, -23.48 ppm).

B5) ^{1}H NMR spectrum for [(HPNP)CoCl(H)D] (**2-HD**).

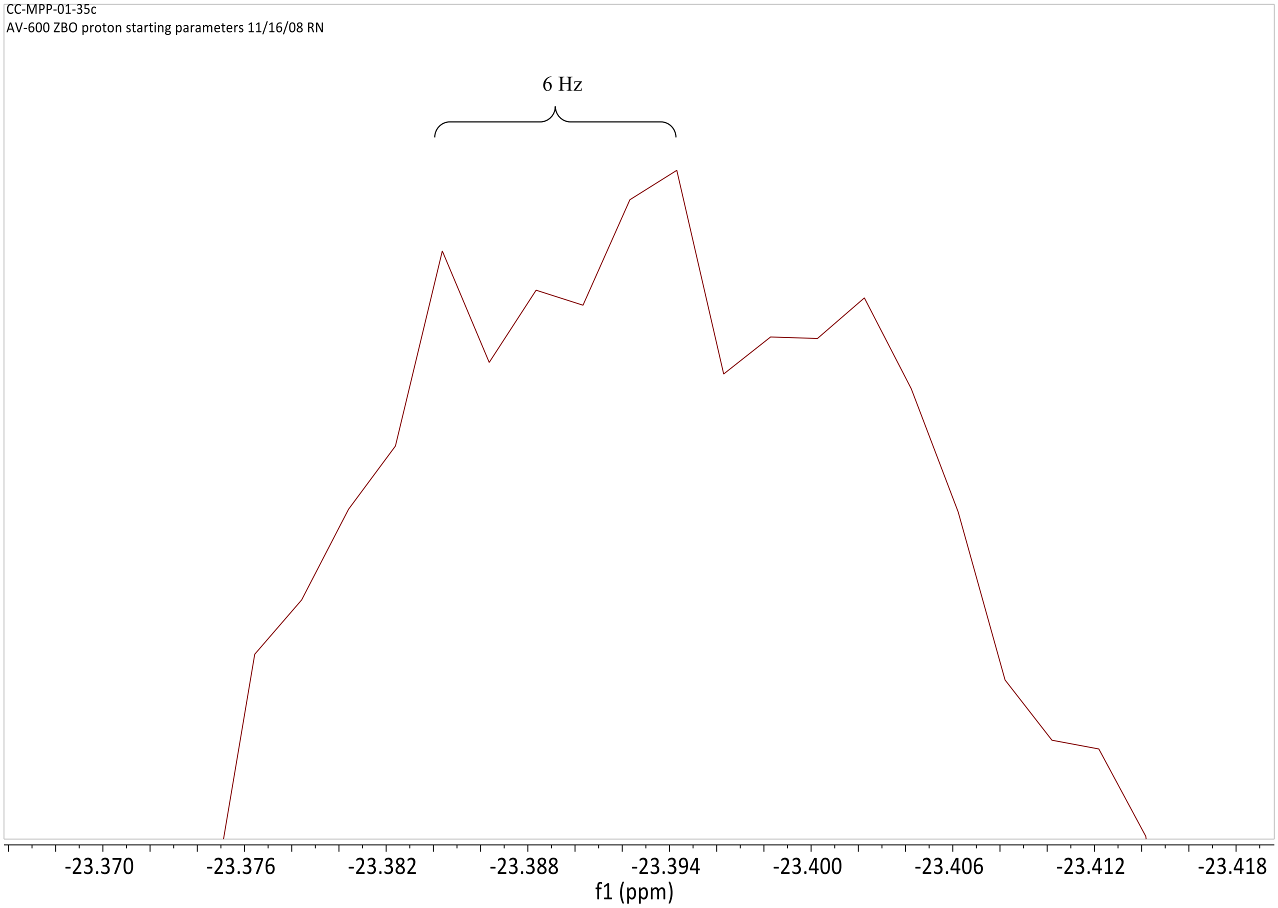

Figure 6.: ^{1}H NMR spectrum ($C_6D_5CD_3$, -80˚C, 600 MHz) for [(HPNP)CoCl(H)D] (**2-HD**) showing the H – D coupling constant (6 Hz).

B6) UV-Vis data for **1**/**2** equilibrium

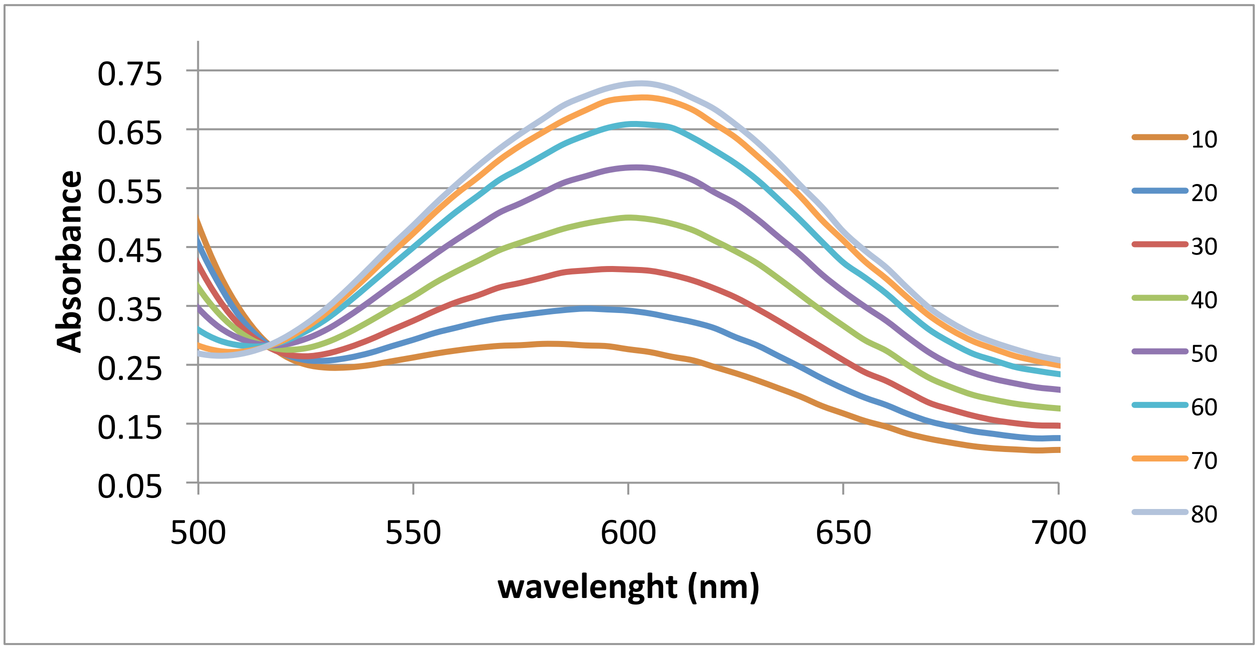

Figure 7. UV-Vis spectra for the equilibrium between **1** and 2 at different temperatures (range10˚C to 80˚C) [H_2] = 1 atm. Absorbance measured at 605 nm for [**1**].

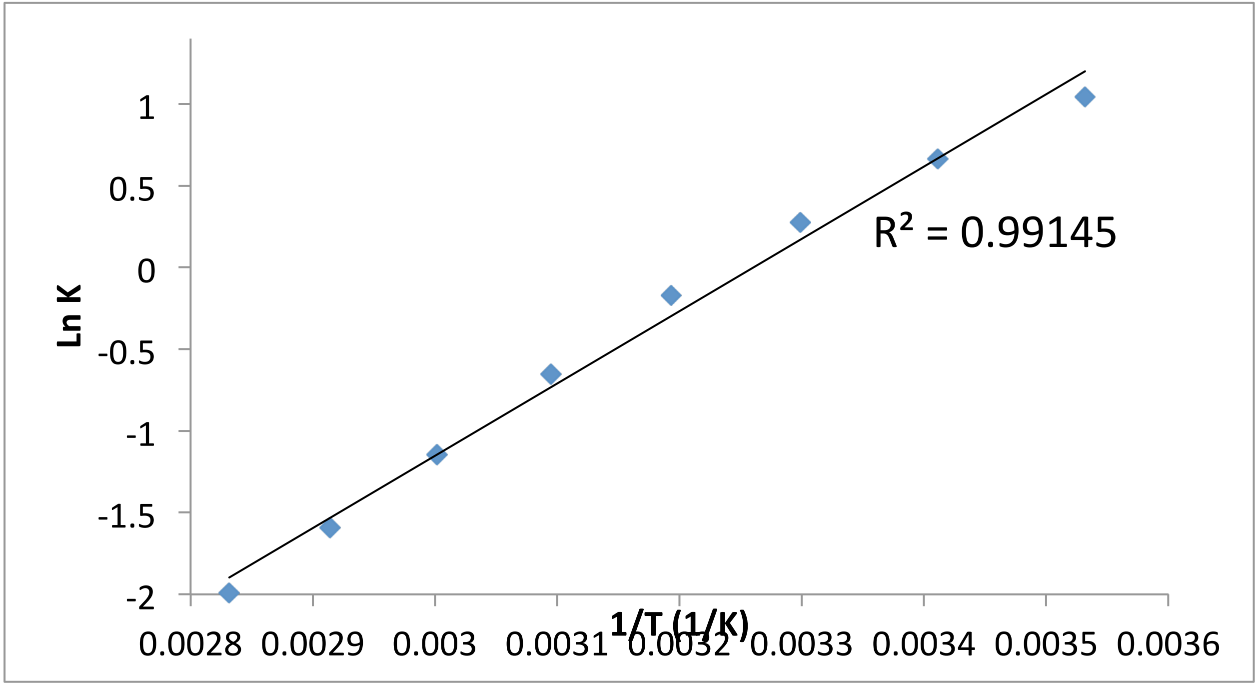

Figure 8. Van't Hoff plot for the reaction of [(HPNP)CoCl] (**1**) with H_2.

B7) T_1 vs. Temperature plot for [(HPNP)CoCl(H)$_2$] (**2**)

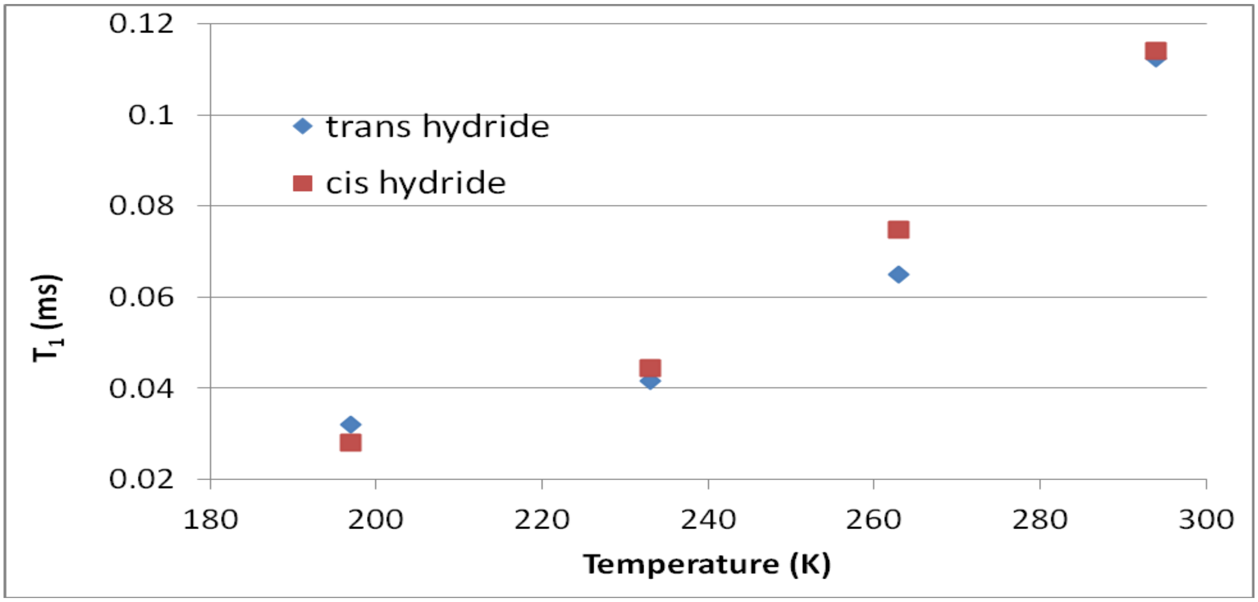

Figure 9. T_1 vs. Temperature plot for the hydride resonances in [(HPNP)CoCl(H)$_2$] (**2**). Blue: hydride *trans* to Cl; red: hydride *cis* to Cl.

C1) ^{1}H NMR spectrum for [(PNP)Co]$_2$ (**3**)

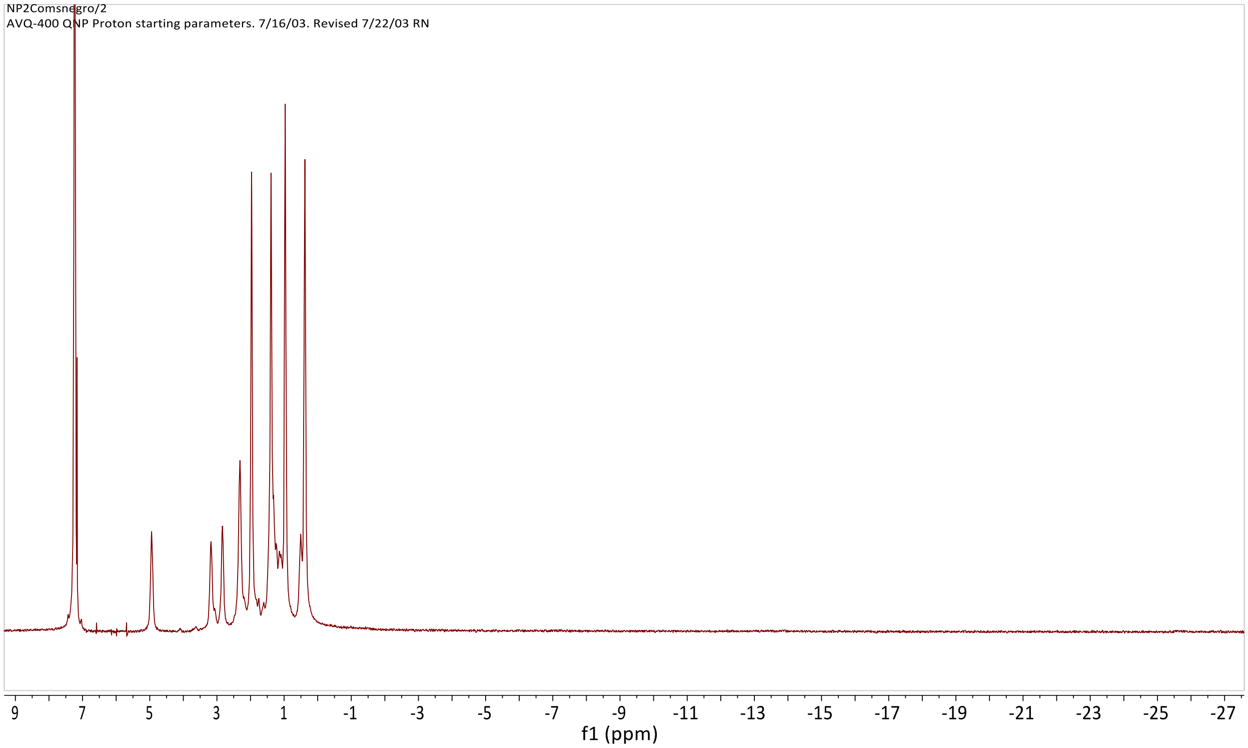

Figure 10. ^{1}H NMR spectrum (C_6D_6, 20°C, 400 MHz) for [(PNP)Co]$_2$ (**3**).

C2) ^{1}H NMR spectra for [(PNP)CoH]$_2$ (**4**)

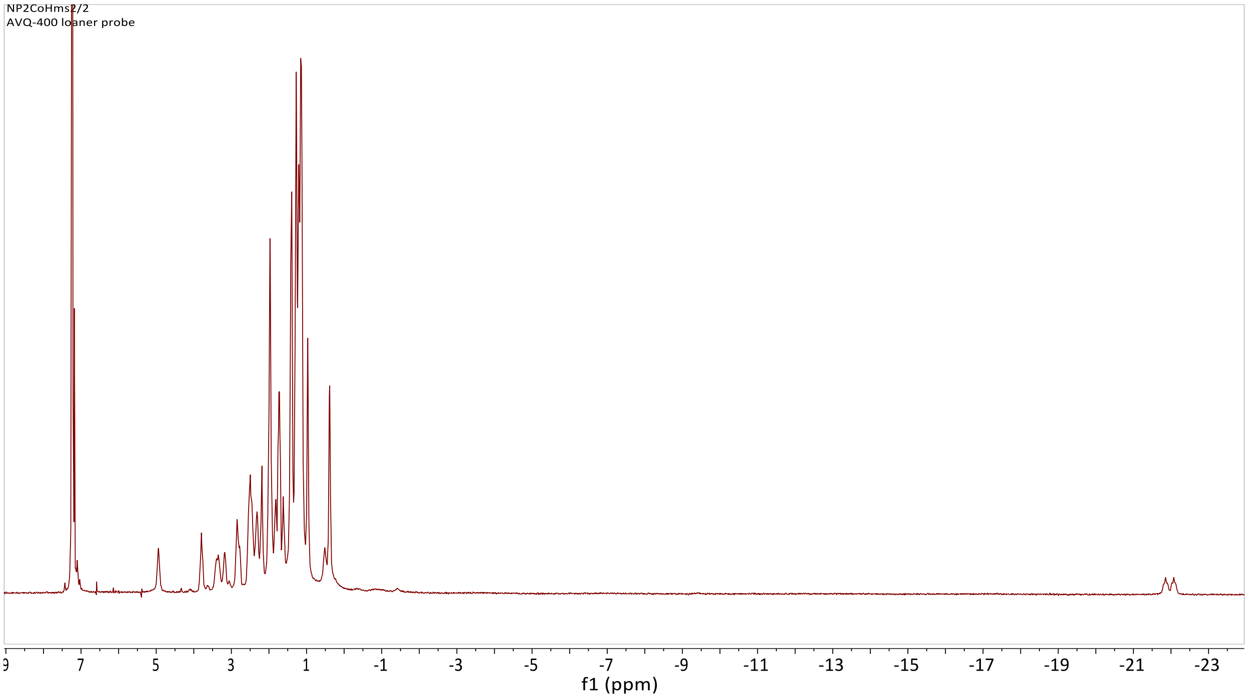

Figure 11. ^{1}H NMR spectrum (C_6D_6, 20°C, 400 MHz) for [(PNP)CoH]$_2$ (**4**).

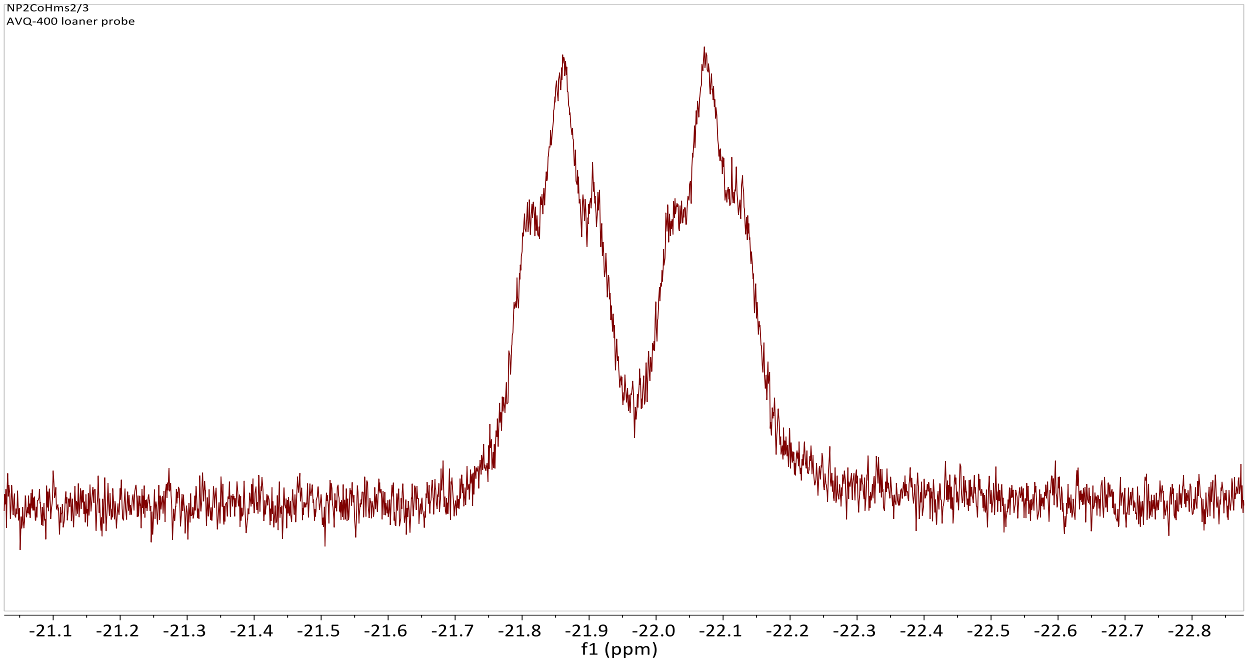

Figure 12. ^{1}H NMR spectrum (C_6D_6, 20°C, 400 MHz) for the hydride resonance in [(PNP)CoH]$_2$ (**4**).

C3) ^{1}H NMR and ^{2}H NMR spectra for [(PNP)CoD]$_2$ (**4-D$_2$**)

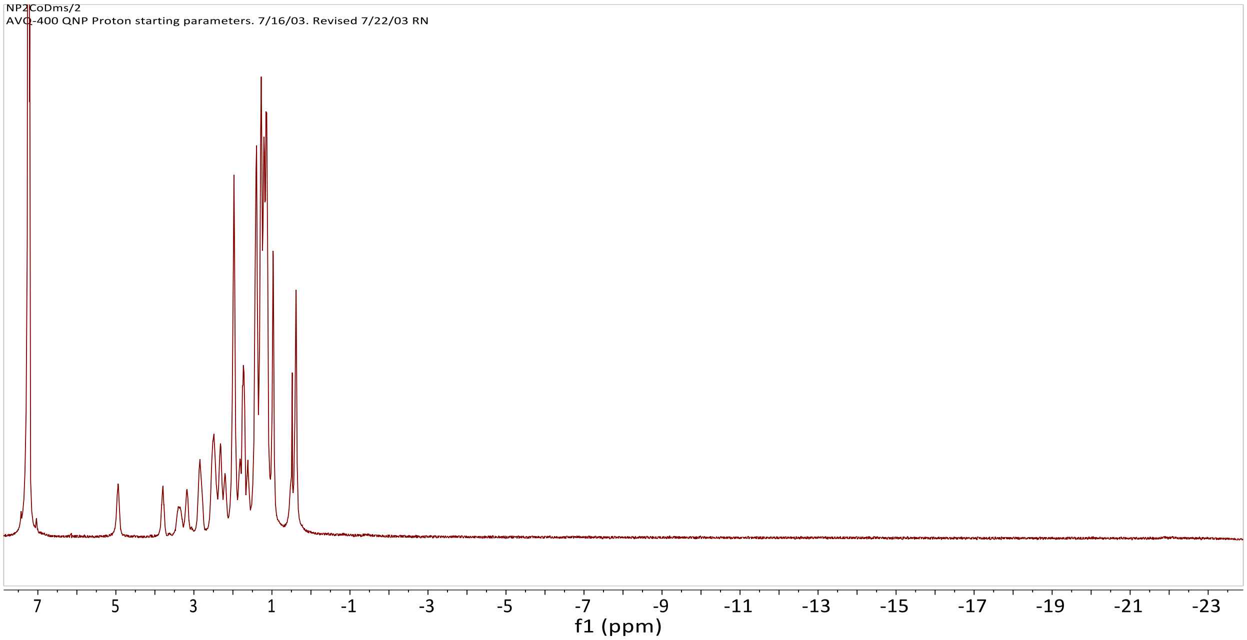

Figure 13. ^{1}H NMR (C_6D_6, 20˚C, 400 MHz) for [(PNP)CoD]$_2$ (**4-D$_2$**).

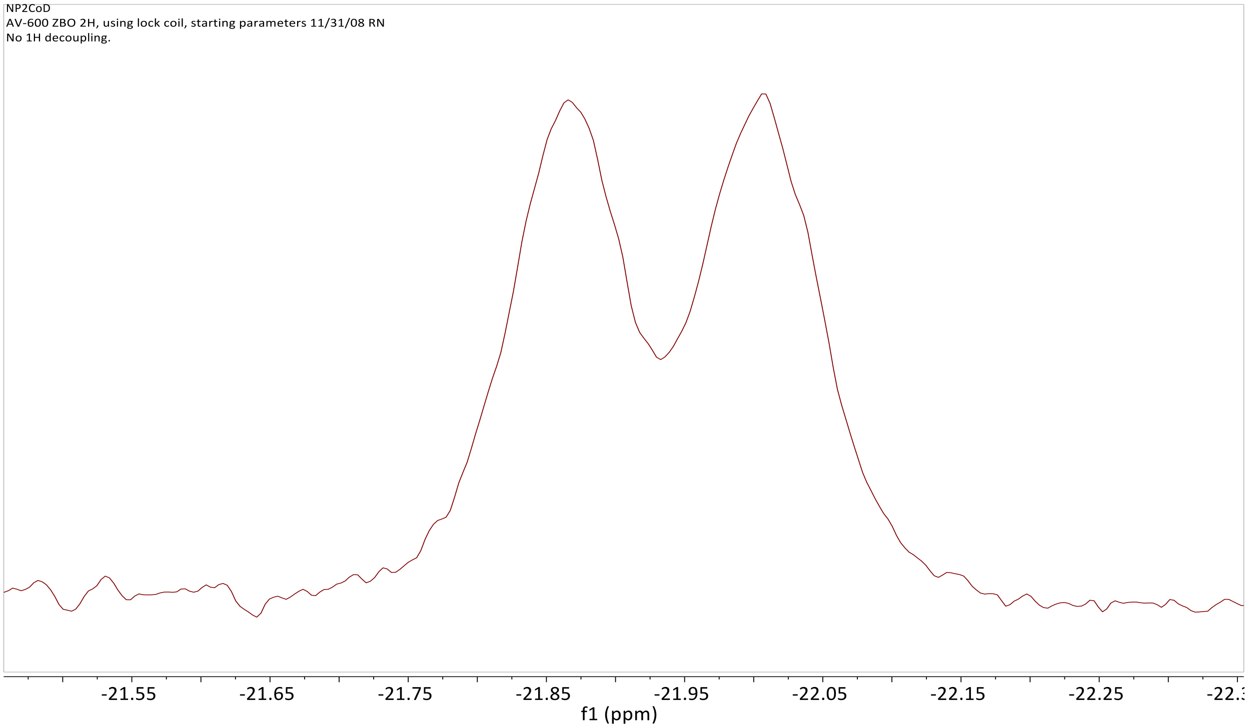

Figure 14. ^{2}H NMR (C_6D_6, 20˚C, 92.12 MHz) for the deuteride resonance in [(PNP)CoD]$_2$ (**4-D$_2$**).

C4) IR spectra for **4** and **4-D₂**.

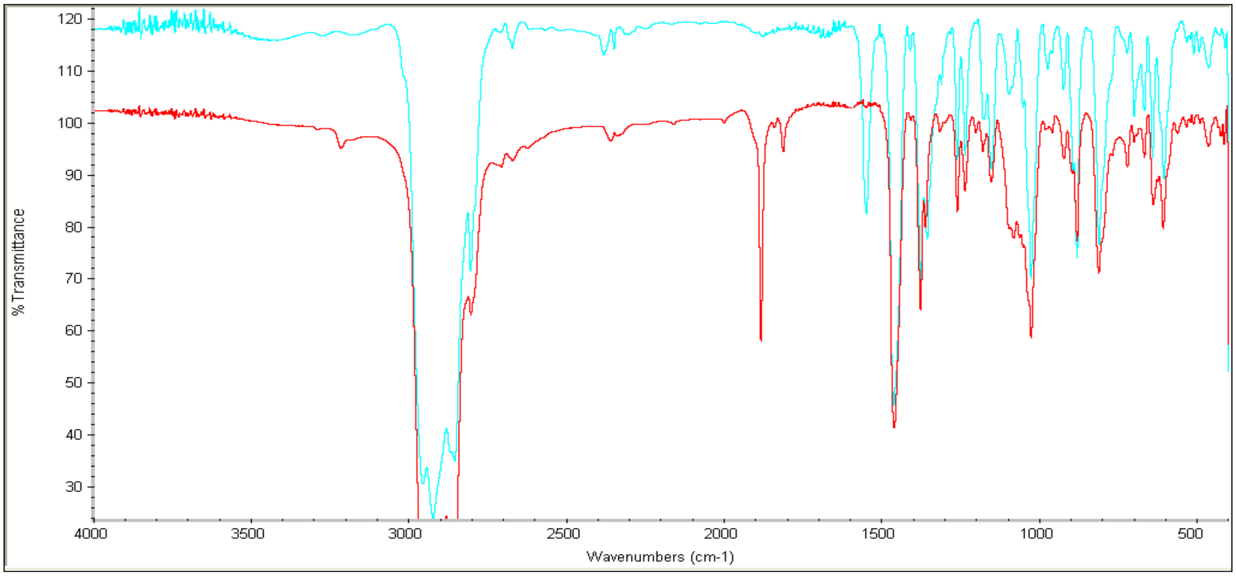

Figure 15. Comparative IR spectra for **4** and **4-D$_2$**. The signals at 1883 and 1548 were assigned to the Co-H and Co-D stretches. Red: **4** (Co – H); green: **4-D$_2$** (Co – D).

C5) T_1 vs. Temperature plot for $[(PNP)CoH]_2$ (**4**)

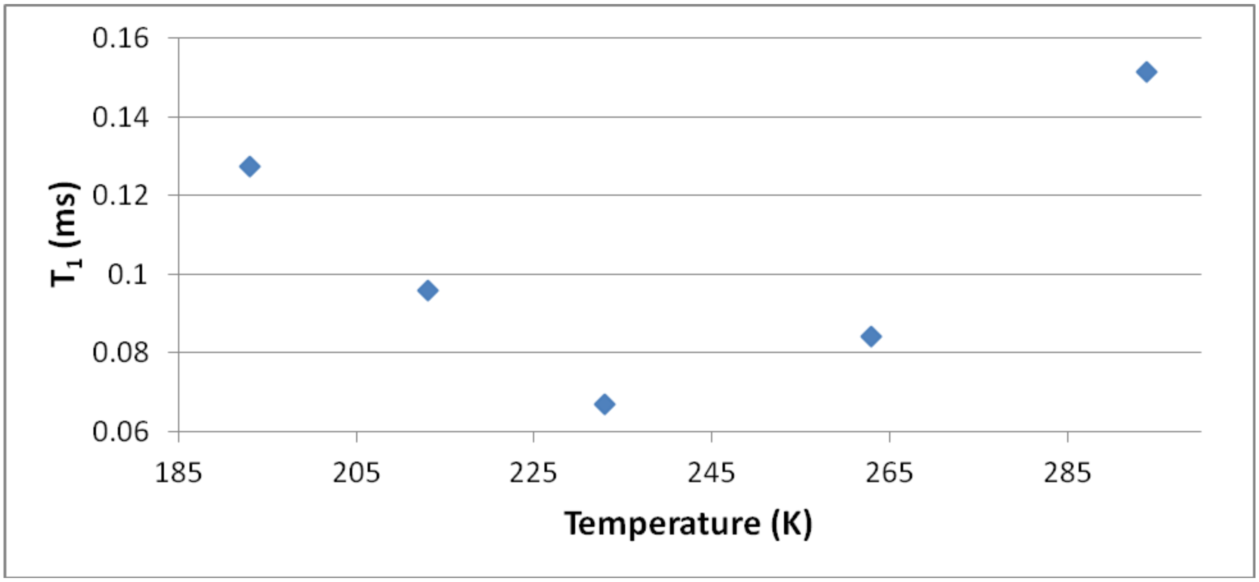

Figure 16. T_1 vs. Temperature plot for $[(PNP)CoH]_2$ (**4**).

D1) ORTEP for [(PNP)CoCO] (**5**)

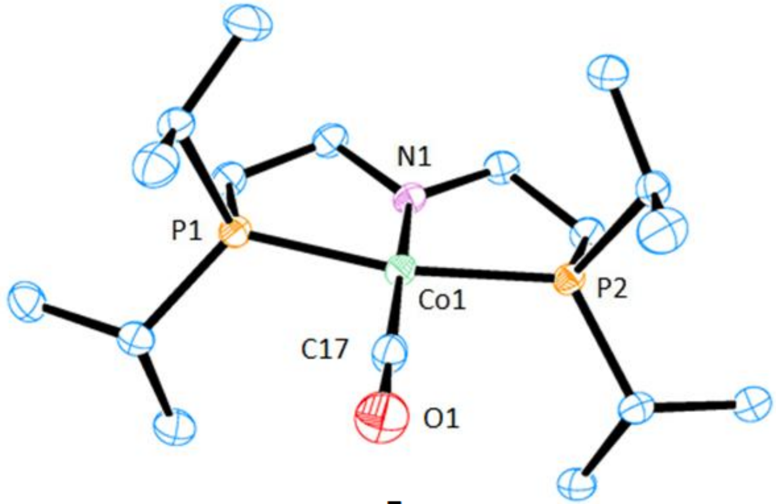

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Figure 17: Thermal ellipsoid (50 %) plot of [(PNP)CoCO] (**5**). Hydrogen atoms have been omitted for clarity.

E1) ^{1}H NMR spectra for [(HPNP)Co(H)$_3$] (**7**)

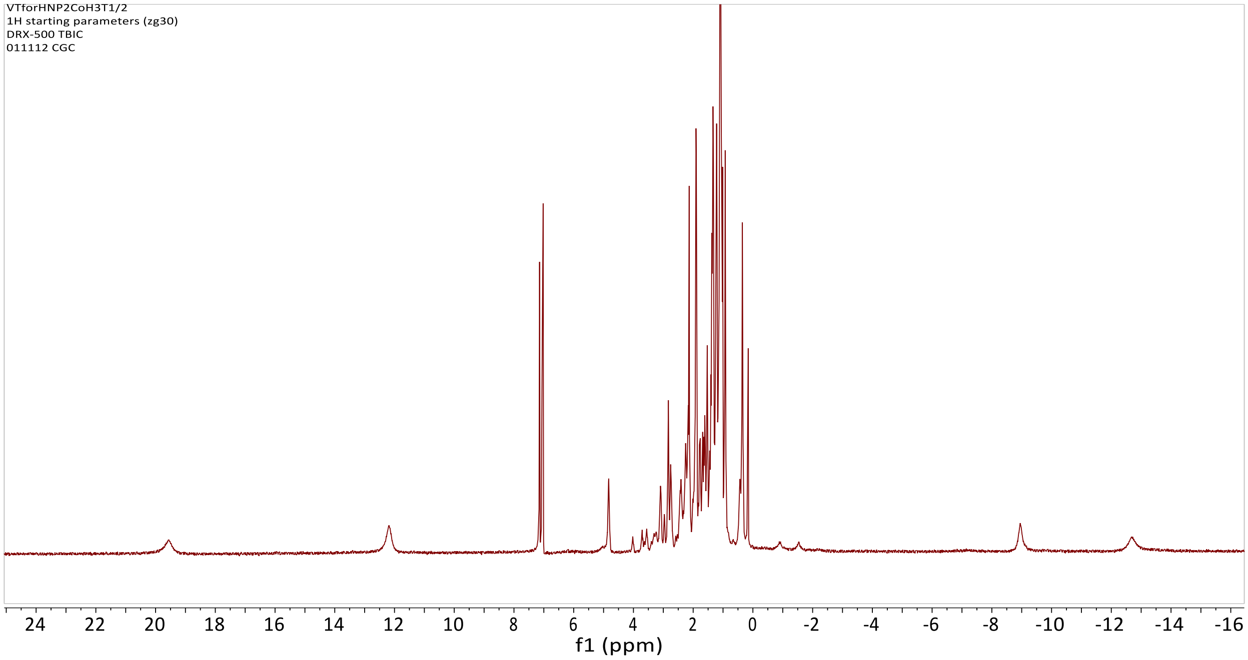

Figure 18. ^{1}H NMR spectrum ($C_6D_5CD_3$, 20°C, 500 MHz) for [(HPNP)Co(H)$_3$] (**7**).

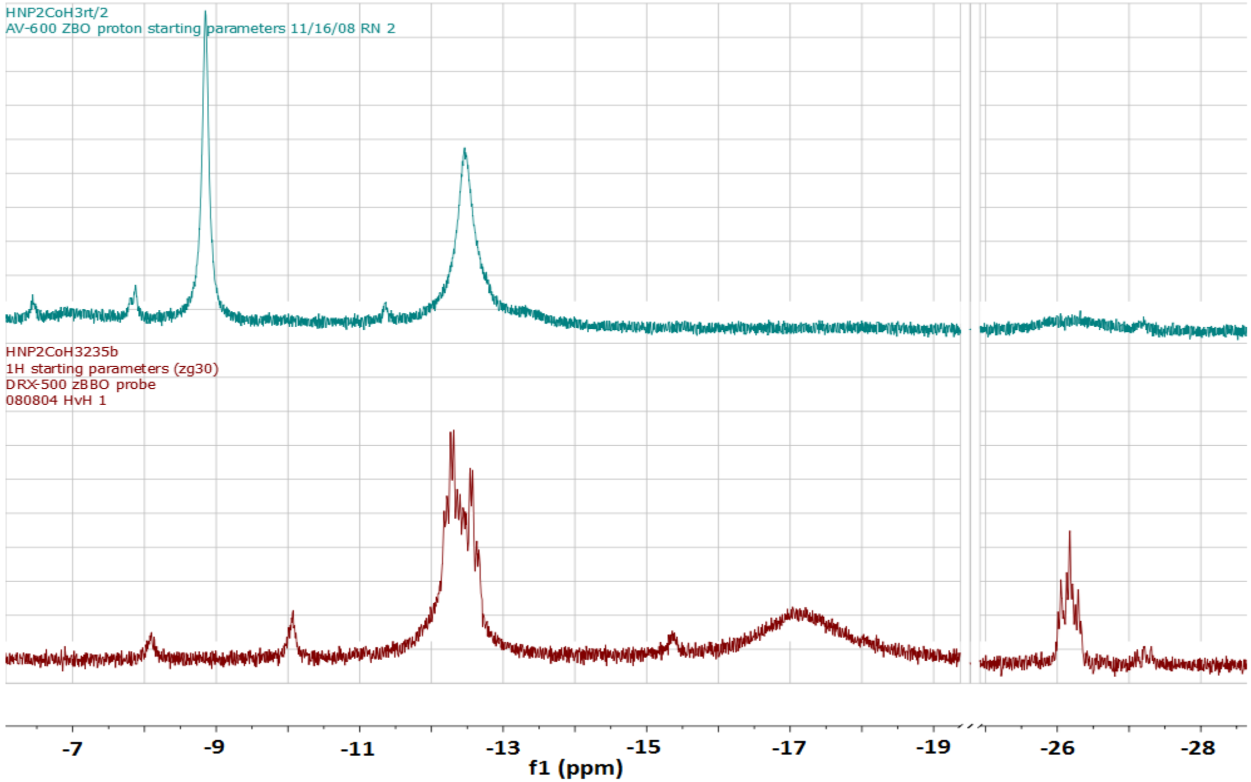

Figure 19. ^{1}H NMR spectra ($C_6D_5CD_3$, 500 MHz) for [(HPNP)Co(H)$_3$] (**7**) at two different temperatures. Top: 20 ˚C; bottom: -40 ˚C.

E2) ^{2}H NMR spectrum for [(DPNP)Co(D)$_3$] (**7-D$_2$**)

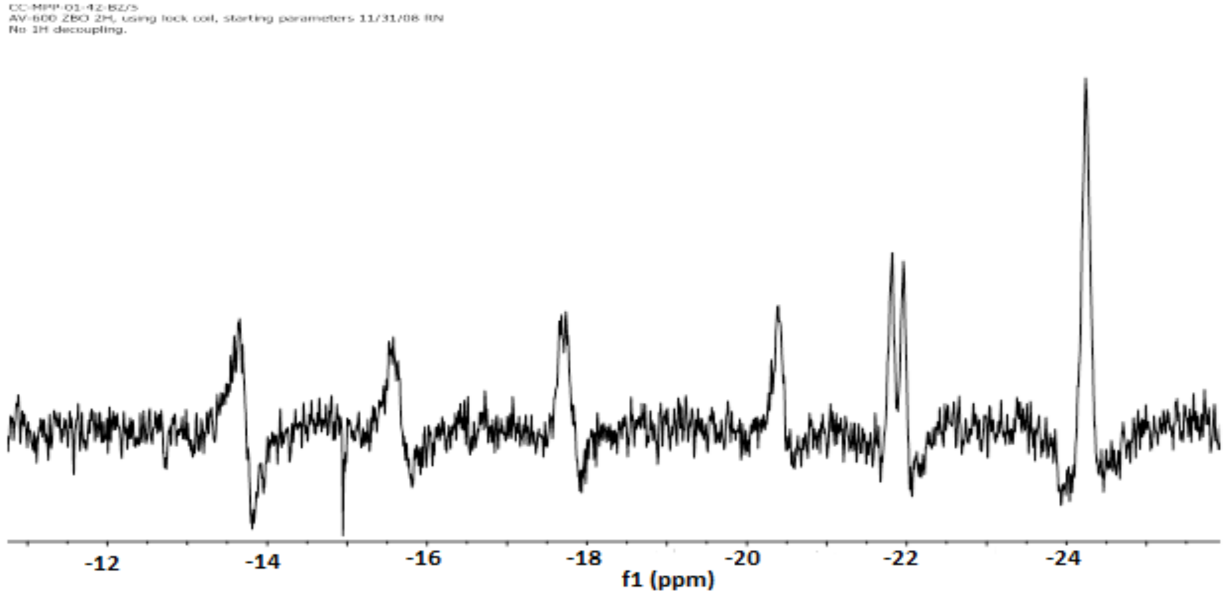

Figure 20. ^{2}H NMR spectrum ($C_6D_5CD_3$, 20˚C, 92.12 MHz) for [(DPNP)Co(D)$_3$] (**7-D$_2$**).

E3) $^{1}H\ \{^{31}P\}$ NMR spectrum for [((H/D)PNP)Co(H/D)$_3$] (**7-HD**)

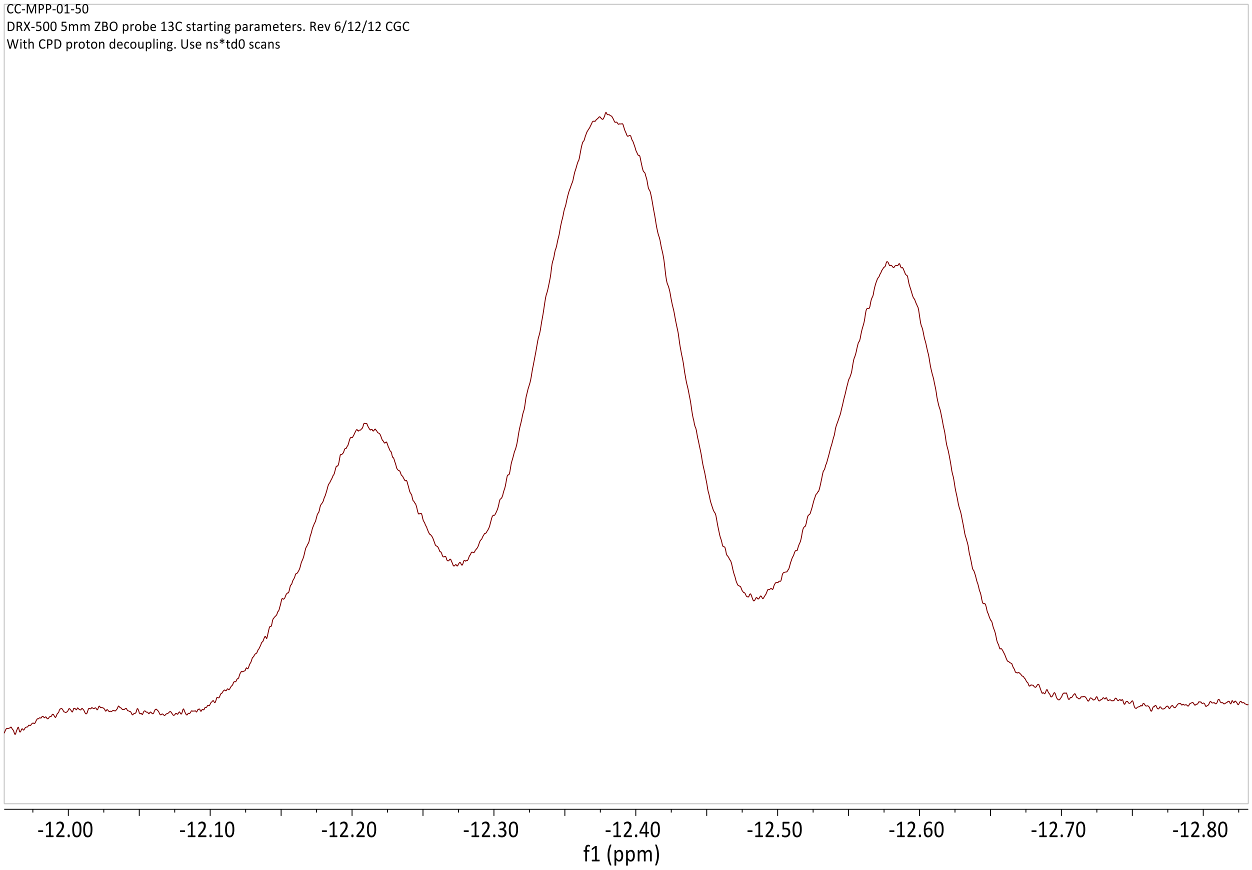

Figure 21. $^{1}H\ \{^{31}P\}$ NMR spectrum ($C_6D_5CD_3$, -80°C, 500 MHz) for [((H/D)PNP)Co(H/D)$_3$] (**7-HD**). The resonances were assigned to the species [(H/D)PNPCoHD$_2$], [(H/D)PNPCo(H)$_3$] and [(H/D)PNPCoH$_2$D].

F1) Table 1: Crystal data and structure refinement for **2**, **4**, **5** and **7**.

	2	**4**	**5**	**7**
Chemical Formula	$C_{16}H_{39}ClCoNP_2$	$C_{32}H_{72}Co_2N_2P_4$	$C_{17}H_{36}CoNOP_2$	$C_{16}H_{40}CoNP_2$
FW (g/mol)	401.80	726.66	391.34	367.36
T (K)	149(2)	163(2)	100(2)	100(2)
Space group	P-1	P-1	P-1	C 2/c
a (Å)	10.526(6)	9.7022(16)	7.6066(8)	19.9694(6)
b (Å)	15.026(8)	12.226(2)	8.4996(9)	7.4326(3)
c (Å)	15.316(8)	17.863(3)	17.1584(17)	13.6932(5)
α (deg)	62.877(7)	108.791(3)	82.406(1)	90
β (deg)	86.128(8)	95.504(2)	82.8630(11)	98.027(1)
γ (deg)	85.906(8)	102.746(2)	69.241(1)	90
V (Å^3)	2149(2)	1924.4(6)	1024.63(18)	2012.49(13)
Z	4	2	2	4
λ (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	1.068	1.051	0.995	1.005
# unique reflections	7961	7053	3748	1833
R_{int}	0.0363	0.0608	0.0241	0.0217
R [I > 2sigma(I)]	0.0420	0.0499	0.0281	0.0336
$R(F_0)$*	0.0516	0.0972	0.0332	0.0364
$R_w(F_0)$*	0.1096	0.1275	0.0722	0.0886
G. of. F.	1.123	1.020	1.045	1.056

G1) Zero Point Energy diagram for B3LYP-311 calculations

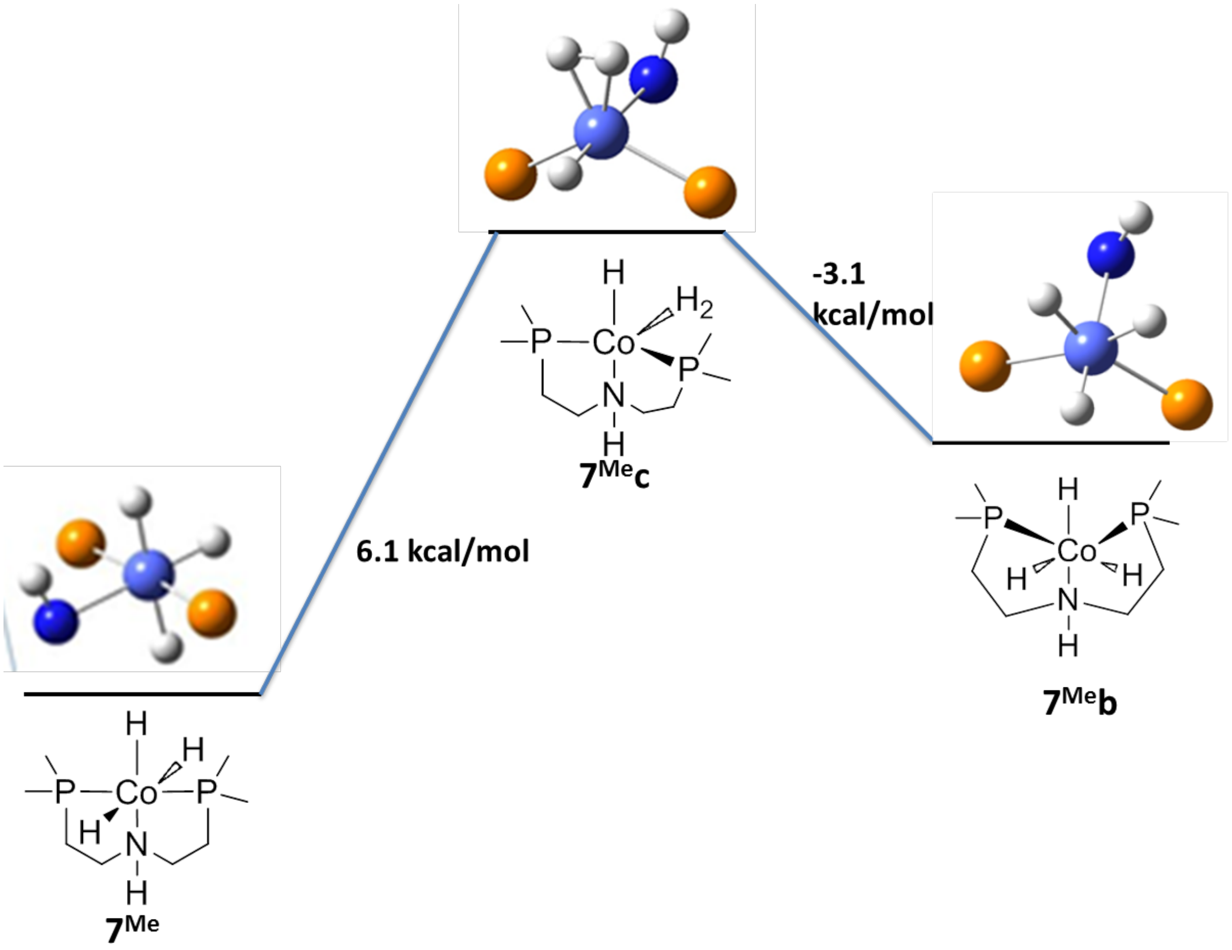

Figure 22. Zero point energy calculations for the proposed equilibria of **7** observed in solution with B3LYP-311 functional.

G2) DFT calculation coordinates and energies.

TPSS

mer-[(HPNP)CoH$_3$] (**7**$^{\mathbf{Me}}$)

E (a.u.) = -2439.296977
ZPE (a.u.) = 0.305176
Charge 0, Multiplicity = 1

C	-0.00003700	-0.51925800	0.03432500
P	2.12186400	-0.47810700	0.03683200
P	-2.12194600	-0.47801500	0.03678200
N	-0.00004000	1.48803300	-0.36519600
H	-0.00038500	1.52558800	-1.39048600
C	-1.24379000	2.15033100	0.13072500
H	-1.29824700	3.19484500	-0.22359000
H	-1.16981600	2.15450300	1.22461300
C	-2.47442100	1.34617000	-0.31652100
H	-2.62075700	1.45132100	-1.40232000
H	-3.38141800	1.72467500	0.17484600
C	2.47441300	1.34586800	-0.31747300
H	3.38160400	1.72442000	0.17351400
H	2.62043100	1.45058400	-1.40334900
C	1.24402700	2.15035800	0.12989300
H	1.17050900	2.15506400	1.22381000
H	1.29845600	3.19471100	-0.22489500
H	0.00002400	-1.97966000	0.30044100
H	-0.00038700	-0.26485600	1.55303900
H	0.00022300	-0.85933200	-1.47027500
C	3.03141100	-1.28390600	-1.31809000
H	4.07496300	-1.06605700	-1.22621400
H	2.88222600	-2.34226600	-1.26790100
H	2.67177800	-0.91713400	-2.25672800
C	3.07883900	-0.83364400	1.54354800
H	2.97278000	-1.86758300	1.79776000
H	4.11145400	-0.61298500	1.37058900
H	2.71489800	-0.22939000	2.34811300
C	-3.07852500	-0.83488300	1.54343400
H	-4.11503500	-0.64072800	1.36218200
H	-2.94987900	-1.86246300	1.81256200
H	-2.73304700	-0.21126700	2.34133500
C	-3.03164200	-1.28278400	-1.31865100
H	-2.90087300	-2.34290700	-1.25589500
H	-4.07221300	-1.04646600	-1.23949600
H	-2.65666200	-0.93211300	-2.25743700

Fac-[(HPNP)CoH$_3$] (**7**$^{\mathbf{Me}}$**b**)

E (a.u.) = -2439.293279
ZPE (a.u.) = 0.305690
Charge 0, Multiplicity = 1

Co	-0.01604600	-0.11001200	-1.03670900
H	-0.93333000	0.35510800	-2.13216200
H	0.93380200	0.31423500	-2.11867500
H	-0.04452800	-1.38090800	-1.79292500
C	-0.92668000	1.97145900	0.90211500
H	-1.06612700	3.04681200	1.10580800
H	-0.47992500	1.51753700	1.79661900
C	1.44996400	2.16460300	0.14672700
H	1.45108900	3.10774800	0.72028100
H	1.97614100	2.33041100	-0.79963500
C	-2.25700600	1.27860700	0.57616000
H	-2.75147500	1.78317000	-0.26634000
H	-2.93549900	1.31444000	1.44113700
C	2.13990900	1.03677800	0.93416600
H	3.21972800	1.23011300	1.00519000
H	1.75200500	0.98356100	1.96192200
C	-3.36607500	-1.00204900	-0.88862100
H	-3.25632600	-2.05321100	-1.18191600
H	-4.27383600	-0.89125500	-0.27948800
H	-3.44934300	-0.40337200	-1.80200000
C	-2.07161900	-1.43717400	1.61136300
H	-3.09754900	-1.35571800	1.99801500
H	-1.84396300	-2.49440200	1.42657500
H	-1.37280000	-1.06990900	2.37327300
C	3.30535200	-0.98056700	-0.85806100
H	4.18221000	-1.04995700	-0.19905800
H	3.17187600	-1.93217100	-1.38678100
H	3.46234000	-0.20074400	-1.61129400
C	1.93164700	-1.80900700	1.48863400
H	1.15124200	-1.62995300	2.23750100
H	1.80178600	-2.82677400	1.09994100
H	2.91765200	-1.73618700	1.96898100
N	0.04797600	1.77408800	-0.22008100
P	-1.83865900	-0.47412800	0.02266500
P	1.74509700	-0.59894000	0.07748200
H	-0.24727300	2.35327900	-1.01036000

[(HPNP)Co(H)H$_2$] (**7**$^{\mathbf{Me}}$**c**)

E (a.u.) = -2439.287804
ZPE (a.u.) = 0.304268
Charge 0, Multiplicity = 1

Co	-0.02275500	-0.22871600	-0.93175100
H	-0.46725000	0.14201000	-2.38620600
H	0.49925800	0.12156100	-2.36593800
H	-0.06334400	-1.65893300	-1.35076400
C	-0.89402000	1.96345000	0.87486100
H	-0.98687300	3.04592700	1.07037300
H	-0.43288700	1.49743300	1.75443900
C	1.44324400	2.17243500	0.02319400
H	1.43101700	3.14945700	0.53714600

H	1.94014100	2.29717300	-0.94591400
C	-2.25523100	1.31558500	0.59590900
H	-2.77267400	1.84953300	-0.21530200
H	-2.89547400	1.36115200	1.48920900
C	2.18271700	1.11061600	0.85267200
H	3.25779000	1.33868500	0.88604200
H	1.81922700	1.10052100	1.89021800
C	-3.48428300	-0.86810300	-0.89705600
H	-3.42799100	-1.91199500	-1.22977200
H	-4.37780200	-0.74074500	-0.26883000
H	-3.56396200	-0.23469600	-1.78808600
C	-2.20040000	-1.44050200	1.56479500
H	-3.21935800	-1.31496100	1.95994400
H	-2.03150300	-2.50145800	1.34185400
H	-1.47443500	-1.13937700	2.32993000
C	3.38822100	-0.93615300	-0.85922400
H	4.27318200	-0.95087000	-0.20608000
H	3.28633000	-1.91212900	-1.34975200
H	3.52034200	-0.18160300	-1.64367500
C	2.06864400	-1.72164000	1.52216700
H	1.29727300	-1.53366700	2.27843600
H	1.95459600	-2.75554300	1.17308600
H	3.06335600	-1.60752000	1.97712400
N	0.03863700	1.72437300	-0.27918500
P	-1.90845100	-0.44439800	0.00574900
P	1.80992900	-0.57003200	0.07263400
H	-0.30056100	2.28708500	-1.06556500

B3LYP

mer-[(HPNP)CoH$_3$] (**7^{Me}**)

E (a.u.) = -2439.393126
ZPE (a.u.) = 0.307696
Charge 0, Multiplicity = 1

C	0.00000000	-0.54320400	-0.01658500
P	2.14059800	-0.46477500	0.01879200
P	-2.14059900	-0.46477500	0.01879200
N	0.00000000	1.52352800	-0.37642200
H	-0.00000100	1.56310100	-1.39337100
C	-1.24184900	2.15626700	0.12357400
H	-1.31612700	3.20257100	-0.20629100
H	-1.17941700	2.15114700	1.21452200
C	-2.46072900	1.35068800	-0.33849100
H	-2.59046400	1.45301200	-1.42136000
H	-3.37444000	1.72106000	0.13569600
C	2.46073000	1.35068700	-0.33849300
H	3.37444100	1.72105900	0.13569100
H	2.59046200	1.45300900	-1.42136300
C	-3.08001300	-0.78096600	1.57764000
H	-4.14924200	-0.57772900	1.46702000
C	-3.19919600	-1.33099900	-1.22088900
H	-2.80777900	-1.13145000	-2.21918200
C	1.24185000	2.15626700	0.12357200
H	1.17941900	2.15114800	1.21452000
H	1.31612800	3.20257000	-0.20629400
C	3.19919600	-1.33100200	-1.22088700
H	2.80777900	-1.13145400	-2.21918100
C	3.08001300	-0.78096400	1.57764000
H	4.14924200	-0.57772600	1.46702100
H	0.00000000	-1.99656200	0.23133300
H	-0.00000300	-0.30338900	1.50557400
H	-0.00000100	-0.85488600	-1.52768400
H	3.13180000	-2.40673000	-1.04448200
H	4.24746400	-1.02397900	-1.16113100
H	-3.13180100	-2.40672800	-1.04448600
H	-4.24746400	-1.02397600	-1.16113200
H	-2.93880800	-1.82602200	1.86173500
H	-2.66296600	-0.16341400	2.37406500
H	2.93880800	-1.82601900	1.86173800
H	2.66296600	-0.16341000	2.37406500

Fac-[(HPNP)CoH$_3$] (**7^{Me}b**)

E (a.u.) = -2439.388366
ZPE (a.u.) = 0.308189
Charge 0, Multiplicity = 1

Co	-0.01439900	-0.13993300	-1.07190100
H	-0.94834800	0.29882700	-2.15196600
H	0.93879800	0.26515500	-2.14478000
H	-0.03771700	-1.43195200	-1.77421800
C	-0.95044300	1.99063700	0.86362300
H	-1.11350000	3.06121000	1.04984500
H	-0.52409700	1.56983200	1.77854400
C	1.42832900	2.17104100	0.15772100
H	1.43213100	3.10367600	0.73962200
H	1.96755000	2.35566000	-0.77260000
C	-2.26670900	1.28083400	0.53768500
H	-2.75125400	1.75870800	-0.31908000
H	-2.95617800	1.33772000	1.38603900
C	2.12144400	1.04602100	0.93858600
H	3.19150800	1.25423500	1.03213400
H	1.72202500	0.97825900	1.95541600
C	-3.38885900	-1.03410600	-0.84432100
H	-3.28110700	-2.09005400	-1.10200400
H	-4.28966300	-0.90471300	-0.23762200
H	-3.47886000	-0.47110500	-1.77366200
C	-2.07400300	-1.39381700	1.64786400
H	-3.08547600	-1.29473900	2.05342300
H	-1.86059100	-2.45321700	1.48697900
H	-1.35909900	-1.01800300	2.38333500
C	3.34808600	-0.94569900	-0.82852200
H	4.21610800	-0.99784400	-0.16478000
H	3.23769300	-1.89657400	-1.35441000
H	3.49899000	-0.17021300	-1.58024500
C	1.96408200	-1.79280100	1.49767300
H	1.16266100	-1.63792100	2.22246700
H	1.87141400	-2.80910700	1.10757100
H	2.92956300	-1.69695800	2.00340600
N	0.04271000	1.79035400	-0.22361500

P	-1.86509600	-0.48109400	0.03736300
P	1.78184600	-0.59485900	0.08868200
H	-0.23555400	2.34146800	-1.02931300

[(HPNP)Co(H)H_2] (**7^{Me}c**)

E (a.u.) = -2439.383423
ZPE (a.u.) = -2439.383423
Charge 0, Multiplicity = 1

Co	-0.02134100	-0.27562400	-0.94097100
H	-0.44567900	0.06497600	-2.42553000
H	0.46412700	0.05046400	-2.41046300
H	-0.05551000	-1.71678500	-1.31424900
C	-0.92243900	1.99176500	0.81870500
H	-1.03926600	3.07169800	0.98775200
H	-0.48470000	1.56760800	1.72523700
C	1.42391500	2.17723900	0.02827000
H	1.41393900	3.14649700	0.54695800
H	1.93799900	2.31815200	-0.92492200
C	-2.26881500	1.32522600	0.53710500
H	-2.76990800	1.82368500	-0.29972500
H	-2.92727500	1.40512800	1.40822200
C	2.16245600	1.12043500	0.85707400
H	3.22708900	1.36650100	0.91887200
H	1.78069300	1.09504900	1.88214700
C	-3.50723900	-0.90014600	-0.86056900
H	-3.45680000	-1.95300500	-1.14770000
H	-4.39734300	-0.74291200	-0.24305500
H	-3.58505400	-0.30936700	-1.77496900
C	-2.21968500	-1.38223900	1.60878500
H	-3.22937100	-1.23866200	2.00724700
H	-2.05896900	-2.44691200	1.42336900
H	-1.48881600	-1.06227300	2.35443000
C	3.43192100	-0.88221900	-0.84152900
H	4.31210600	-0.87025000	-0.19039500
H	3.36068600	-1.85732300	-1.32899500
H	3.54586500	-0.13033400	-1.62487800
C	2.12280100	-1.70424100	1.52485600
H	1.34091300	-1.54298700	2.26949200
H	2.04154700	-2.73555600	1.17367100
H	3.10351600	-1.56584500	1.99101700
N	0.03517000	1.73998300	-0.29446200
P	-1.93654600	-0.45081300	0.01978500
P	1.84873800	-0.56430500	0.08195100
H	-0.28013400	2.27627100	-1.09830800

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