Well-Defined Cobalt(I) Dihydrogen Catalyst: Experimental Evidence for a Co(I)/Co(III) Redox Process in Olefin Hydrogenation.

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General Considerations. All manipulations of air- and moisture-sensitive compounds were carried out in the absence of water and dioxygen in an MBraun inert atmosphere drybox under a dinitrogen atmosphere except where specified otherwise. All glassware was oven dried for a minimum of 8 h and cooled in an evacuated antechamber prior to use in the drybox. Solvents for sensitive manipulations were dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves purchased from Strem following a literature procedure prior to use.¹ Chloroform-d, toluene- d_8 and benzene- d_6 were purchased from Cambridge Isotope Labs and were degassed and stored over 4 Å molecular sieves prior to use. Lithium hexamethyldisilazane was purchased from Sigma-Aldrich and recrystallized from toluene under an inert atmosphere prior to use. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150°C prior to use in a glovebox. NMR Spectra were recorded at room temperature on a Varian spectrometer operating at 500 MHz (¹H NMR) and 126 MHz (¹³C NMR) (U500, VXR500, UI500NB) and referenced to the residual CHCl₃, C_7D_7H and C_6D_5H resonance (δ in parts per million, and J in Hz). Potassium graphite (KC₈)² and Schwartz's reagent $(Cp_2ZrHCl (Cp = cyclopentadienyl))^3$ were prepared according to literature procedures. T₁ relaxation times were determined by using the standard inversion recovery pulse sequence method.

Synthesis of Metal Complexes

Preparation of (^{Mes}CCC)Co(N₂)(PPh₃) (1-N₂): A 20 mL scintillation vial was charged with (^{Mes}CCC)CoCl₂py (0.094 g, 0.124 mmol) and THF (10 mL). A suspension of KC₈ (0.035 g, 0.259 mmol) in THF (5 mL) was added to the mixture. After stirring for 2 hours, the dark brown suspension was filtered over Celite and to the filtrate, PPh₃ (0.033 g, 0.124 mmol) was added, resulting in the change of the mixture to dark red. The THF was removed under reduced pressure after stirring the solution for 1 h. The product was then extracted into benzene (3 x 5 mL), filtered over Celite and concentrated under reduced pressure to a red solid. The solid was triturated with hexane (10 mL) and concentrated *in vacuo* to give a fine red powder (0.097 g, 0.109 mmol, 88%). NMR data (in toluene-*d*₈, 25 °C): ¹H δ = 7.72 (d, J = 8.0, 2H), 7.33 (d, J = 7.5, 2H), 7.16 (t, J = 7.0, 1H), 7.12 (d, J = 8.0, 2H), 6.89 (t, J = 7.5, 2H), 6.87-6.81 (m, 7H), 6.77-6.68 (m, 12H), 6.52 (d, J = 7.5, 2H), 2.03 (s, 6H), 1.92 (s, 6H), 1.62 (s, 6H) The ¹H and ¹³C NMR spectra in benzene *d*₆ match that of the reported compound.⁴

Preparation of (^{Mes}CCC)Co(H₂)(PPh₃) (1-H₂). A solution of 1-N₂ (0.005 g, 0.006 mmol) in *ca*. ¹/₂ mL of benzene-d₆ or toluene-d₈ was transferred to a J. Young tube and sealed. The sample was subjected to three freeze-pump-thaw cycles and exposed to 1 atm of H₂ at 77K and then allowed to warm ambient temperature resulting a color change of the solution to red-orange after agitating the mixture. After subjecting 1-H₂ to a freeze-thump-thaw cycle, the Co(n^2 -H₂) complex was unchanged. Upon exposure to an N₂ atmosphere, the gradual formation of 1-N₂ was observed by ¹H NMR and the solution turned dark red. Elemental analysis or HRMS (ESI) were not performed since upon exposure to N₂, the H₂ ligand dissociates from the complex. NMR data (in benzene- d_6 , 25 °C): ¹H δ = 7.80 (d, J = 7.5, 2H), 7.52 (d, J = 7.0, 2 H), 7.39 (m, 2 H), 7.31 (d, J= 7, 1H), 7.10 (t, J = 7.5, 2 H), 7.04 (m, 2H), 6.97-6.88 (m, 7H) 6.86-6.82 (m, 2H), 6.80-6.75 (m, 6H), 6.66 (s, 2H), 6.54 (d, J = 7.5, 2H), 2.13 (s, 6H), 1.89 (s, 6H), 1.36 (s, 6H), -5.48 (s, 2H). ¹³C δ = 144.7, 139.3, 139.1, 137.9, 137.7, 137.7, 137.7, 136.9, 135.3, 133.1, 133.0, 132.7, 129.8, 129.2, 128.0, 127.6, 121.6, 121.5, 118.8, 109.5, 108.6, 105.9, 21.1, 19.0, 17.4. NMR data (in toluene- d_8 ,

25 °C): ${}^{1}\text{H} \delta = 7.76 \text{ (d, J} = 7.5, 2\text{H}), 7.42 \text{ (d, J} = 7.0, 2\text{H}), 7.32 \text{ (s, 2H)}, 7.22 \text{ (t, J} = 6.5, 2\text{H}), 6.90-6.80 \text{ (m, 12H)}, 6.77-6.71 \text{ (m, 8H)}, 6.64 \text{ (s, 2H)}, 6.48 \text{ (d, J} = 10, 2\text{H}), 2.14 \text{ (s, 6H)}, 1.82 \text{ (s, 6H)}, 1.30 \text{ (s, 6H)}, -5.56 \text{ (s, 2H)}.$

Preparation of (^{Mes}CCC)Co(D₂)(PPh₃) (1-D₂). A solution of 1-N₂ (0.008 g, 0.009 mmol) in *ca*. ¹/₂ mL of toluene-d₈ or toluene was transferred to a J. Young tube and sealed. The sample was subjected to three freeze-pump-thaw cycles and exposed to 1 atm of D₂ at 77K and allowed to warm to ambient temperature for 15 min. After agitating the mixture, the color of the solution turned orange. ¹H NMR data (in toluene-*d*₈, 25 °C): $\delta = 7.76$ (d, J = 7.5, 2H), 7.42 (d, J = 7.0, 2H), 7.22 (t, J = 6.5, 1H), 6.90-6.80 (m, 13H), 6.77-6.71 (m, 8H), 6.64 (s, 2H), 6.48 (d, J = 10, 2H), 2.14 (s, 6H), 1.82 (s, 6H), 1.30 (s, 6H). ²H NMR data (in toluene, 76.7 MHz, 25 °C): $\delta = -5.66$ (s, 2H).

Preparation of (^{Mes}CCC)Co(HD)(PPh₃) (1-HD). A solution of 1-N₂ (0.005 g, 0.006 mmol) in *ca.* ½ mL of toluene-*d*₈ was transferred to a J. Young tube and sealed. The sample was subjected to three freeze-pump-thaw cycles and exposed to 1 atm of HD (generated from excess LiAlH₄ and degassed D₂O*) at 77K and let stand for 10 min at ambient temperature upon which the solution slowly turned red-orange. ¹H NMR data (in toluene-*d*₈, 25 °C): δ = 7.76 (d, J = 7.5, 2H), 7.42 (d, J = 7.0, 2H), 7.32 (s, 2H), 7.22 (t, J = 6.5, 1H), 6.90-6.80 (m, 12H), 6.77-6.71 (m, 7H), 6.64 (s, 2H), 6.48 (d, J = 7.5, 2H), 2.14 (s, 6H), 1.82 (s, 6H), 1.30 (s, 6H), -5.56 (t, J = 33, ½ H) -5.60 (t, J = 33, ½ H). (*This is very exothermic and it is vital that this is carried out with no oxygen gas present).

Alternative preparation of 1-HD. A solution of 1-N₂ (0.005 g, 0.006 mmol) in *ca.* ½ mL of benzene-d₆ was transferred to a J. Young tube and sealed. The sample was subjected to three freeze-pump-thaw cycles and exposed to a mixture of H₂ and D₂ (50:50) at 1 atm and 77K. The solution was warmed to ambient temperature and upon agitating the reaction mixture the color of the solution turned red-orange. ¹H NMR data (in benzne-*d*₆, 25 °C): $\delta = \delta = 7.80$ (d, J = 7.5, 2H), 7.52 (d, J = 7.0, 2 H), 7.39 (m, 2 H), 7.31 (d, J= 7, 1H), 7.10 (t, J = 7.5, 2 H), 7.04 (m, 2H), 6.97-6.88 (m, 7H) 6.86-6.82 (m, 2H), 6.80-6.75 (m, 6H), 6.66 (s, 2H), 6.54 (d, J = 7.5, 2H), 2.13 (s, 6H), 1.89 (s, 6H), 1.36 (s, 6H), -5.46 (t, J = 33, ½ H), -5.49 (t, J = 33, ½ H).

Preparation of (^{Mes}CCC)Co(N₂)(PMe₃) (2-N₂): A 20 mL scintillation vial was charged with (^{Mes}CCC)CoCl₂py (0.222 g, 0.294 mmol) and THF (10 mL). A suspension of KC₈ (0.087 g, 0.647 mmol) in THF (5 mL) was added to the mixture. After stirring for 2 hours, the dark brown suspension was filtered over Celite and to the filtrate PMe₃ (1.0 M in THF, 0.30 mL, 0.30 mmol), was added, resulting in the change of the mixture to dark red. After stirring the solution for 1 h, the THF was removed under reduced pressure. The solid was taken up in Et₂O (3 x 5 mL), filtered over Celite, concentrated under pressure and triturated with hexanes (10 mL) to yield a red powder (0.160 g, 0.225 mmol, 77%). Crystals suitable for X-ray diffraction were grown from slow evaporation of a concentrated solution of complex **2-N**₂ in hexanes at room temperature. NMR data (in benzene-*d*₆, 25 °C): ¹H δ = 7.87 (d, J = 7.5, 2H), 7.71 (d, J = 7.5, 2H), 7.46 (t, J = 7.5, 1H), 7.10 (t, J = 7.5, 2H), 6.95 (t, J = 7.8, 2H), 6.83 (s, 2H), 6.72 (s, 2H), 6.62 (d, J = 7.5, 2H), 2.10 (s, 6H), 2.09 (s, 6H), 2.02 (s, 6H), 0.45 (d, J_{CH3-P} = 6.5, 9H). ¹³C δ = 209.6, 163.0, 143.1, 138.4, 138.4, 138.2, 135.8, 134.4, 132.2, 130.2, 128.9, 121.8, 121.7, 118.6, 109.7, 108.3, 105.6, 21.1, 18.5, 18.4, 15.6, 15.4. IR: 2114 cm⁻¹ (N₂). HRMS (ESI), calc. for C₄₁H₄₂CoN₄P (M – N₂)⁺:

calculated 680.2479; found 680.2507.

Preparation of (^{Mes}CCC)Co(H₂)(PMe₃) (2-H₂): A solution of 2-N₂ (0.006 g, 0.008 mmol) in *ca*. ¹/₂ mL of benzene-*d*₆ was transferred to a J. Young tube and sealed. The sample was subjected to two freeze-pump-thaw cycles and exposed 1 atm of H₂ at 77K. The reaction was warmed to room temperature for 10 min and after agitating the mixture, the color of the solution turned red. ¹H NMR data (in benzene-*d*₆, 25 °C): 7.88 (d, J = 8.5, 2H), 7.78 (d, J = 7.5, 2 H), 7.52 (t, J = 7.0, 1H), 7.09 (s, 2H), 6.93 (t, J = 8.0, 2H), 6.74 (s, 2H), 6.72 (s, 2H), 6.54 (d, J = 7.5, 2H), 2.02 (s, 6H), 1.97 (s, 6H), 1.96 (s, 6H), 0.56 (d, J_{CH3-P} = 6.5, 9H), -5.77 (s, 2H). ¹³C δ = 144.2, 137.7, 137.5, 135.6, 135.3 134.9, 134.2, 132.4, 130.0, 129.1. 128.7, 121.4, 121.3, 118.1, 109.4, 108.2, 105.4, 21.1, 19.4, 19.2, 18.8, 18.5, 18.3. Elemental analysis or HRMS (ESI) were not performed since upon exposure to N₂, the H₂ ligand dissociates from the complex. *T*₁ (minimum): 14 ms (298K).

Preparation of (^{Mes}CCC)Co(D₂)(PMe₃) (2-D₂): A solution of 2-N₂ (0.008 g, 0.011 mmol) in *ca*. ¹/₂ mL of benzene or benzene-*d*₆ was transferred to a J. Young tube and sealed. The sample was subjected to two freeze-pump-thaw cycles and exposed 1 atm of D₂ at 77K. The reaction was warmed to room temperature for 10 min and after agitating the mixture, the color of the solution turned red. ¹H NMR data (in benzene-*d*₆, 25 °C): 7.88 (d, J = 8.5, 2H), 7.78 (d, J = 7.5, 2 H), 7.52 (t, J = 7.0, 1H), 7.09 (s, 2H), 6.93 (t, J = 8.0, 2H), 6.74 (s, 2H), 6.72 (s, 2H), 6.54 (d, J = 7.5, 2H), 2.02 (s, 6H), 1.97 (s, 6H), 1.96 (s, 6H), 0.56 (d, J_{CH3-P} = 6.5, 9H). ²H NMR data (in benzene, 76.7 MHz, 25 °C): -5.86.

Preparation of (^{Mes}CCC)Co(HD)(PMe₃) (2-HD): A solution of 2-N₂ (0.009 g, 0.013 mmol) in *ca.* $\frac{1}{2}$ mL of benzene- d_6 was transferred to a J. Young tube and sealed. The sample was subjected to two freeze-pump-thaw cycles and exposed to a mixture of D₂ and H₂ gas (0.5:0.5 atm) at 77K. The reaction was warmed to room temperature for 10 min and after agitating the mixture, the color of the solution turned red. ¹H NMR data (in benzene- d_6 , 25 °C) 7.88 (d, J = 8.5, 2H), 7.78 (d, J = 7.5, 2 H), 7.52 (t, J = 7.0, 1H), 7.09 (s, 2H), 6.93 (t, J = 8.0, 2H), 6.74 (s, 2H), 6.72 (s, 2H), 6.54 (d, J = 7.5, 2H), 2.02 (s, 6H), 1.97 (s, 6H), 1.96 (s, 6H), 0.56 (d, J_{CH3-P} = 6.5, 9H), -5.75 (t, J = 32, $\frac{1}{2}$ H), -5.79 (t, J = 32, $\frac{1}{2}$ H).

Preparation of (^{Mes}CCC)Co(H)(Cl)(PMe₃) (3-HCl). A 20 mL scintillation vial charged with 2-N₂ (0.024 g, 0.034 mmol) and *ca*. 5 mL of THF was cooled to -35°C. A solution of HCl•Et₂O (2.0 M, 17 μ L, 0.034 mmol) was added and the mixture was stirred for 1 h. Following the removal of the volatiles under reduced pressure, the mixture was washed with Et₂O (2 x 5 mL), dissolved in C₆H₆ (10 mL), filtered over a plug of Celite and the solvent was removed *in vacuo* to give an orange solid (0.020 g, 0.027 mmol, 80%). Crystals suitable for X-ray diffraction were grown from slow evaporation of a concentrated solution of complex **3-HCl** in Et₂O at room temperature. ¹H NMR data (in benzene-*d*₆): δ = 7.76 (d, J = 7.5, 2H), 7.45 (d, J = 7.5, 2H), 7.32 (t, ²J = 6.5 1H), 7.08 (t, J = 7.3, 2H), 6.95-6.88 (m, 4H), 6.75 (d, J = 7.5, 2H) s (2H), 2.30 (s, 6H), 2.06 (s, 6H), 2.03 (s, 6H), 0.55 (d, J_{CH3P} = 7, 9H), -10.0 (d, ²J_{HP} = 109, 1H). ¹³C δ = 146.3, 138.5, 138.1, 137.9, 133.8, 131.5, 130.3, 123.1, 122.8, 122.1, 110.6, 110.4, 107.3, 21.1, 19.0, 18.9, 14.0, 13.8. *T*₁ (minimum) resonance at -10.0 ppm: 139 ms (298K). HRMS (ESI), calc. for C₄₁H₄₂ClCoN₄P (M – H)⁺: calculated 715.2168; found 715.2161.

Preparation of (MesCCC)Co(D)(Cl)(PMe3) (3-DCl). A 20 mL scintillation vial charged with 2-

N₂ (0.023 g, 0.032 mmol) and *ca*. 5 mL of THF was cooled to -35°C. A solution of DCl•Et₂O (1.0 M, 32 µL, 0.033 mmol) was added and the mixture was stirred for 1 h. Following the removal of the volatiles under reduced pressure, the mixture was washed with Et₂O (2 x 5 mL), dissolved in C₆H₆ (10 mL), filtered over a plug of Celite and the solvent was removed *in vacuo* to give an orange solid (0.019 g, 0.027 mmol, 82%).. ¹H NMR data (in benzene-d₆): δ = 7.76 (d, J = 7.5, 2H), 7.45 (d, J = 7.5, 2H), 7.32 (t, J = 6.5 1H), 7.08 (t, J = 7.3, 2H), 6.95-6.88 (m, 4H), 6.75 (d, J = 7.5, 2H) s (2H), 2.30 (s, 6H), 2.06 (s, 6H), 2.03 (s, 6H), 0.55 (d, ²J_{CH3P} = 7, 9H). ²H NMR data (in benzene, 76.7 MHz, 25 °C): δ = -10.0 (d_{DP}, ²J = 16.4, 1H).

Preparation of (^{Mes}CCC)Co(Cl)₂(PMe₃) (3-Cl₂). A 20 mL scintillation vial charged with 2-N₂ (0.0273 g, 0.0385 mmol) in *ca*. 5 mL of THF. A solution of ClCPh₃ (0.0220 g, 0.0789 mmol) in *ca*. 5 mL of THF was added to the mixture. After stirring the brown solution for 1 h, the THF was removed under reduced pressure. The solid residue was washed with THF (5 mL x 2) over a pad of Celite and the orange solid was dissolved in DCM (15 mL). Following the removal of solvent under reduced pressure, the solid residue was triturated with hexanes (5 mL) and dried *in vacuo* to yield an orange solid (0.0103 g, 0.0137 mmol, 36%). ¹H NMR data (in benzene-*d*₆): δ = 7.68 (d, J = 8.0, 2H), 7.40 (d, J = 7.5, 2H), 7.27 (t, J = 8, 1H), 7.05 (t, J = 7.5, 2H), 6.94-6.89 (m, 4H), 6.75 (d, J = 8, 2H), 6.68 (s, 2H), 2.58 (s, 6H), 2.13 (s, 6H), 1.94 (s, 6H), 0.40 (d, ²J_{CH3P} = 11, 9H). ¹³C (NMR data in CDCl₃) δ = 147.7, 138.8, 138.5, 138.0, 133.2, 133.1, 131.7, 130.43, 128.6, 125.2, 124.1, 123.7, 111.6, 109.7, 21.4, 20.1, 19.7, 16.4, 16.1. HRMS (ESI), calc. for C₄₁H₄₂ClCoN₄P (M – Cl)⁺: calculated 715.2168; found 715.2164.

Stoichiometric Reactivity of 3-HCl

Reactivity with HCl: HCl•Et₂O (2.0 M, 6 μ L, 0.0012 mmol) was added to a J. Young tube containing **3-HCl** (0.009 g, 0.012 mmol) and ½ mL C₆D₆ then sealed. The resulting ¹H NMR spectrum showed resonances corresponding to the formation of H₂ gas and **3-Cl**₂.

Reactivity with Cp₂ZrHCl: Cp₂ZrHCl (6 mg, 0.023 mmol) was added to a J. Young tube containing **3-HCl** (0.05 g, 0.008 mmol) and $\frac{1}{2}$ mL C₆D₆ then sealed. The resulting ¹H NMR spectrum showed resonances corresponding to the formation of H₂ gas, Cp₂ZrCl₂ and **2-N**₂.

	(MesCCC)CoCl(H)PMe3	(MesCCC)Co(N2)(PMe3)	
	(3-HCl)	(2-N ₂)	
Bond Distances (Å)			
Co – C1	1.922(3)	1.9033 (19)	
Co – C13	1.857(3)	1.8734(19)	
Co – C20	1.919(3)	1.9079(19)	
Co – Cl1	2.3057(7)	N/A	
Co – H	1.40(5)	N/A	
Co – N	N/A	1.871(2)	
Co – P	2.2229(8)	2.2131(6)	
N - N	N/A	1.022(2)	
Co – Cl2	2.483(6)	N/A	
Bond Angles (°)			
C13-Co-N5	N/A	162.95(8)	
C1-Co-C13	80.77(11)	76.18(8)	
C13-Co-C20	80.76(11)	79.12(8)	
C1-Co-C20	158.71(11)	153.32(8)	
C1-Co-Cl1	99.23(8)	N/A	
N5-Co-P	N/A	101.29(5)	
Р-Со-Н	174.0(17)	N/A	
Cl1-Co-Cl2	89.81(14)	N/A	

Table S1: Selected bond lengths and angles for 2-N₂ and 3-HCl.

Table S2. Crystallographic Parameters for $2\text{-}N_2$ and 3-HCl

	$(MesCCC)Co(N_s)PMos$	(MesCCC)CoUCIDMon
	$(2 N_{\rm c})$	
	$(2-1N_2)$	(3-HCI)
	cd34w	cm07w
Empirical Formula	C41 H42 Co N6 P	C41 H42.18 Cl 1.12 Co N4 P
Formula Weight	708.71	720.66
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 21/n	P 21/c
Unit Cell Dimensions	a = 7.8946(3)Å	a =12.2774(5) Å
	b = 16.5851(5) Å	b = 18.0919(7) Å
	c = 27.3473(10) Å	c = 16.3936(7) Å
	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 94.4478 (12)^{\circ}$	$\beta = 94.5253(17)^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
Volume	3569.9(2) Å ³	3630.0(3) Å ³
Z	4	4
Reflections collected	88825	44035
Independent	7004	
reflections	/884	6670
Goodness-of-fit on F2	1.098	1.016
Final R indices	R1 = 0.0386	R1 = 0.0443
[I>sigma(I)]	wR2 = 0.0870	wR2 = 0.0915

Determination of T1: T_1 (minimum): 12 *ms* (253 to 313K). Measurements were obtained on a 500 MHz spectrometer of **1-H**₂ in toluene- d_8 from 203 K to 343 K by the standard inversion recovery pulse sequence method.



Figure S1. Plot of *T1* as function of Temperature (K)

¹H NMR Spectrum, 500 MHz, C₆D₆ (1-N₂)



Figure S2. ¹H NMR (C₆D₆, 500 MHz) spectrum of (^{Mes}CCC)Co(N₂)(PPh₃) (**1-N**₂).



Figure S3. ¹H NMR (C₇D₈, 500 MHz) spectrum of (MesCCC)Co(N₂)(PPh₃) (**1-N**₂).



Figure S4. ¹H NMR (C₆D₆, 500 MHz) spectrum of (^{Mes}CCC)Co(H₂)(PPh₃) (**1-H**₂).

¹H NMR Spectrum, 126 MHz, C₆D₆ (1-H₂)





¹H NMR Spectrum, 500 MHz, C₇D₈ (1-H₂)





Figure S6. ¹H NMR (C₇D₈, 500 MHz) spectrum of (MesCCC)Co(H₂)(PPh₃) (1-H₂).



Figure S7. ¹H NMR (C₇D₈, 500 MHz) spectrum of (^{Mes}CCC)Co(D₂)(PPh₃) (**1-D**₂).

²H NMR Spectrum, 76.7 MHz, C₇H₈ (1-D₂)





Figure S9. ¹H NMR (C₇D₈, 500 MHz) spectrum of (^{Mes}CCC)Co(HD)(PPh₃) (**1-HD**).



Figure S10. ¹H NMR (C₆D₆, 500 MHz) spectrum of (^{Mes}CCC)Co(HD)(PPh₃) (**1-HD**).



Figure S11. ¹H NMR (C₆D₆, 500 MHz) spectrum of (^{Mes}CCC)Co(N₂)(PPh₃) (**2-N**₂). (*denotes H grease and x denotes hexanes)



Figure S12. ¹³C NMR (C₆D₆, 126 MHz) spectrum of (^{Mes}CCC)Co(N₂)(PPh₃) (**2-N₂**).

¹H NMR Spectrum, 500 MHz, C₆D₆ (2-H₂)



Figure S13. ¹H NMR (C₆D₆, 500 MHz) spectrum of (^{Mes}CCC)Co(H₂)(PMe₃) (**2-H**₂). (* denotes **2**-**N**₂, [^] denotes H grease, ^x denotes hexanes)

¹³C NMR Spectrum, 126 MHz, C₆D₆ (2-H₂)



Figure S14. ¹³C NMR (C₆D₆, 126 MHz) spectrum of (^{Mes}CCC)Co(H₂)(PMe₃) (**2-H**₂). (* denotes hexanes)

¹H NMR Spectrum, 500 MHz, C₆D₆ (2-D₂)



Figure S15. ¹H NMR (C₆D₆, 500 MHz) spectrum of (^{Mes}CCC)Co(D₂)(PMe₃) (**2-D**₂). (* denotes **2**-**N**₂, [^] denotes H grease, ^x denotes hexanes)



Figure S16. ¹H NMR (C₆H₆, 76.7 MHz) spectrum of (^{Mes}CCC)Co(D₂)(PMe₃) (**2-D**₂). (*denotes deuterated benzene)



Figure S17. ¹H NMR (C₆D₆, 500 MHz) spectrum of (^{Mes}CCC)Co(HD)(PMe₃) (**2-HD**).



¹³C NMR Spectrum, 126 MHz, C₆D₆ (3-HCl)



Figure S19. ¹³C NMR (C₆D₆, 126 MHz) spectrum of (^{Mes}CCC)Co(H)Cl(PMe₃) (**3-HCl**).

¹H NMR Spectrum, 500 MHz, C₆D₆ (3-DCl)



Figure S20. ¹H NMR (C₆D₆, 500 MHz) spectrum of (^{Mes}CCC)Co(D)Cl(PMe₃) (**3-DCl**).

²H NMR Spectrum, 76.7 MHz, C₆H₆ (3-DCl)



Figure S21. ²H NMR (C₆H₆, 76.7 MHz) spectrum of (^{Mes}CCC)Co(D)Cl(PMe₃) (**3-DCl**).



grease)

¹³C NMR Spectrum, 126 MHz, CDCl₃ (3-Cl₂)



Figure S23. ¹³C NMR (CDCl₃, 126 MHz) spectrum of (MesCCC)Co(Cl₂)(PMe₃) (3-Cl₂).



Variable Temperature Studies, ¹H NMR Spectra, 500 MHz, 1-H₂ (9 to -2 ppm)



Variable Temperature Studies, ¹H NMR Spectra, 500 MHz, 4-PPh₃-H₂ (9 to -2 ppm)

Figure S26. ¹H NMR (C₇D₈, 500 MHz) spectrum of (^{Mes}CCC)Co(H₂)(PPh₃) (1-H₂). (-50 to -80°C)



Variable Temperature Studies, ¹H NMR Spectra, 500 MHz, 1-H₂ (-4 to -14 ppm)

Figure S27. ¹H NMR (C₇D₈, 500 MHz) spectrum of (MesCCC)Co(H₂)(PPh₃) (1-H₂). (80 to 10°C)



Figure S28. ¹H NMR (C₇D₈, 500 MHz) spectrum of (^{Mes}CCC)Co(H₂)(PPh₃) (1-H₂). (0 to -40°C)





Figure S29. ¹H NMR (C₇D₈, 500 MHz) spectrum of (MesCCC)Co(H₂)(PPh₃) (1-H₂). (-50 to -80°C)



¹H NMR Spectrum, 500 MHz, C₆D₆ (3-HCl reaction with Cp₂ZrHCl)



¹H NMR Spectrum, 500 MHz, C₆D₆ (3-HCl reaction with HCl•Et₂O)





Figure S32. ATR IR Spectrum of (MesCCC)Co(N₂)(PMe₃) (2-N₂).





Figure S33. ATR IR Spectrum of (MesCCC)Co(H)Cl(PMe₃) (3-HCl).

General Procedure for olefin hydrogenation studies. A standard J. Young NMR tube was charged with a solution of olefin, 1,3,5-trimethylbenzene (internal standard) and **1-N**₂ (2 mol%) in *ca.* ¹/₂ ml of benzene-*d*₆. The sample was subjected to two freeze-pump-thaw cycles and H₂ gas (1 atm) was added at 77K on a high-vacuum line. The sample was allowed to warm to ambient temperature, resulting in 4 atm of H₂ gas. The catalytic reaction was monitored by ¹H and ¹³C NMR spectroscopy. Each catalytic experiment was reproduced. Control experiments were carried under similar catalytic conditions. Using (^{Mes}CCC)CoCl₂py (2 mol%) and styrene, no hydrogenation of the olefin was observed. The use of **1-N**₂ (2 mol%) with one drop of Hg displayed similar results for the hydrogenation of styrene.

Hydrogenation with 1-H₂.

A 50 mL schlenk flask charged with $1-N_2$ (0.020 g, 0.0225 mmol) and 5 mL of benzene was subjected to three freeze pump thaw cycles and placed under 1 atm of H₂ gas. Styrene (0.127 mL, 1.105 mmol) was degassed using argon and transferred to the solution of $1-H_2$ via an airtight syringe. The reaction was stirred at room temperature for 2 hours and complete conversion to ethylbenzene was determined using GC-MS.

\bigcirc	$\begin{array}{c} & \begin{array}{c} H_2 (4 \text{ atm}) \\ \end{array} \\ \hline \\ C_6 D_6, \text{ rt, 2 h} \end{array}$	\bigcirc
Entry	Additive	conversion ^a
1	1-N₂ (2 mol%)	>99%
2	1-N₂ (2 mol%) + Hg	>99%
3	(^{Mes} CCC)CoCl ₂ py (2 mol%)	0%
4	1-N₂ (2 mol%) + PPh₃ (10 mol%)	50%
5	1-N₂ (2 mol%) + PPh₃ (25 mol%)	12%
6	1-N₂ (2 mol%) + PPh₃ (50 mol%)	6%
7	2-N₂ (2 mol%)	30%

Table S3. Hydrogenation of styrene control experiments

^aConversion was monitored by ¹H NMR using mesitylene as an internal standard.



Figure S34. ¹H NMR (C₆D₆, 500 MHz) spectrum of **1-N**₂ (2%), mesitylene (*) and styrene under N₂ (top). ¹H NMR spectrum of **1-N**₂ (2%), mesitylene (*) and styrene under 4 atm of H₂ after 2 h (middle). ¹³C NMR spectrum of **1-N**₂ (2%), mesitylene (*) and styrene under 4 atm of H₂ after 2 h (bottom).



Figure S35. ¹H NMR (C₆D₆, 500 MHz) spectrum of **1-N**₂ (2%), mesitylene (*) and octene under N₂ (top). ¹H NMR spectrum of **1-N**₂ (2%), mesitylene (*) and octene under 4 atm of H₂ after 3 h (middle). ¹³C NMR spectrum of **1-N**₂ (2%), mesitylene (*) and octene under 4 atm of H₂ after 3 h (bottom).



Figure S36. ¹H NMR (C₆D₆, 500 MHz) spectrum of **1-N**₂ (2%), mesitylene (*) and hex-5en-2-one under N₂ (top). ¹H NMR spectrum of **1-N**₂ (2%), mesitylene (*) and hex-5-en-2-one under 4 atm of H₂ after 2 h (middle). ¹³C NMR spectrum of **1-N**₂ (2%), mesitylene (*) and hex-5-en-2-one under 4 atm of H₂ after 2 h (bottom).



Figure S37. ¹H NMR (C₆D₆, 500 MHz) spectrum of **1-N**₂ (2%), mesitylene (*) and 2,2dimethylpent-4-enal under N₂ (top). ¹H NMR spectrum of **1-N**₂ (2%), mesitylene (*) and 2,2-dimethylpent-4-enal under 4 atm of H₂ after 22 h (middle). ¹³C NMR spectrum of **1-N**₂ (2%), mesitylene (*) and 2,2-dimethylpent-4-enal under 4 atm of H₂ after 22 h (bottom).



Figure S38. ¹H NMR (C₆D₆, 500 MHz) spectrum of **1-N**₂ (2%), mesitylene (*) and but-3en-1-ol under N₂ (top). ¹H NMR spectrum of **1-N**₂ (2%), mesitylene (*) and but-3-en-1ol under 4 atm of H₂ after 22 h (middle). ¹³C NMR spectrum of **1-N**₂ (2%), mesitylene (*) and but-3-en-1-ol under 4 atm of H₂ after 2 h (bottom).



Figure S39. ¹H NMR (C₆D₆, 500 MHz) spectrum of **1-N**₂ (2%), mesitylene (*) and 4-vinylpyridine under N₂ (top). ¹H NMR spectrum of **1-N**₂ (2%), mesitylene (*) and 4-vinylpyridine under 4 atm of H₂ after 22 h (middle). ¹³C NMR spectrum of **1-N**₂ (2%), mesitylene (*) and 4-vinylpyridine under 4 atm of H₂ after 2 h (bottom).



180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Figure S40. ¹H NMR (C₆D₆, 500 MHz) spectrum of **1-N**₂ (2%), mesitylene (*) and isoprene under N₂ (top). ¹H NMR spectrum of **1-N**₂ (2%), mesitylene (*) and isoprene under 4 atm of H₂ after 21 h (middle). ¹³C NMR spectrum of **1-N**₂ (2%), mesitylene (*) and isoprene under 4 atm of H₂ after 21 h (bottom).



Figure S41. ¹H NMR (C₆D₆, 500 MHz) spectrum of **1-N**₂ (2%), mesitylene (*) and 4-vinylcyclohexene under N₂ (top). ¹H NMR spectrum of **1-N**₂ (2%), mesitylene (*) and 4-vinylcyclohexene under 4 atm of H₂ after 2 h (middle). ¹³C NMR spectrum of **1-N**₂ (2%), mesitylene (*) and 4-vinylcyclohexene under 4 atm of H₂ after 2 h (bottom).



Figure S42. ¹H NMR (C₆D₆, 500 MHz) spectrum of **1**-N₂ (2%), mesitylene (*) and 4-vinylcyclohexene under N₂ (top-blue). ¹H NMR spectrum of **1**-N₂ (2%), mesitylene (*) and 4-vinylcyclohexene under 4 atm of H₂ after 2 h (top-green) at rt.). ¹H NMR spectrum of **1**-N₂ (2%), mesitylene (*) and 4-vinylcyclohexene under 4 atm of H₂ after 19 h (top-red) at 60°C. ¹³C NMR spectrum of**1**-N₂ (2%), mesitylene (*) and 4-vinylcyclohexene under 4 atm of H₂ after 19 h (top-red) at 60°C. ¹³C NMR spectrum of**1**-N₂ (2%), mesitylene (*) and 4-vinylcyclohexene under 4 atm of H₂ after 19 h at 60°C (bottom).



Figure S43. ¹H NMR (C₆D₆, 500 MHz) spectrum of **1-N**₂ (2%), mesitylene (*) and cyclohexene under N₂ (top). ¹H NMR spectrum **1-N**₂(2%), mesitylene (*) and cyclohexene under 4 atm of H₂ after 24 h at 60°C (middle). ¹³C NMR spectrum of **1-N**₂ (2%), mesitylene (*) and cyclohexene under 4 atm of H₂ after 24 h at 60°C (bottom).



Figure S44. ¹H NMR (C₆D₆, 500 MHz) spectrum of **1** (2%), mesitylene (*) and *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride under N₂ (top-teal). ¹H NMR spectrum **1**-N₂ (2%), mesitylene (*) and *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride under 4 atm of H₂ of after 17 h at 60°C (top-red). ²H NMR (C₆H₆, 76.7 MHz) spectrum of **1**-N₂ (2%), mesitylene (*) and *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride under 4 atm of D₂ after 17 h at 60°C (top-red). ¹³C NMR spectrum of **1**-N₂ (2%), mesitylene (*) and *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride under 4 atm of D₂ after 17 h at 60°C (top-red). ¹³C NMR spectrum of **1**-N₂ (2%), mesitylene (*) and *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride under 4 atm of H₂ after 17 h at 60°C (top-red). ¹³C NMR spectrum of **1**-N₂ (2%), mesitylene (*) and *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride under 4 atm of H₂ after 17 h at 60°C (top-red).

Mechanistic Studies

A standard J. Young NMR tube was charged with a solution of styrene ($12 \mu L$, 0.112 mmol) and **1-N**₂ (0.002 g, 0.0022 mmol) in *ca*. $\frac{1}{2}$ ml of benzene-*d*₆. The sample was subjected to two freezepump-thaw cycles and D₂ gas (1 atm) was added at 77K on a high-vacuum line. The sample was allowed to warm to ambient temperature, resulting in 4 atm of D₂ gas. After letting sample sit at room temperature for 1 hour a ¹H NMR was taken (teal-below). Another ¹H NMR was taken after 24 h at room temperature and is shown below in maroon.



Figure S45. ¹H NMR (C₆D₆, 500 MHz) spectrum of **1-N**₂ (2%) and styrene under 4 atm of D₂ after 1 h at room temperature (top). ¹H NMR spectrum of **1-N**₂ (2%) and styrene under 4 atm of D₂ of after 24 h at room temperature (bottom). (* denotes ethylbezne and ^ denotes vinyl protons of styrene)

A standard J. Young NMR tube was charged with a solution of styrene ($12 \mu L$, 0.112 mmol) and **1-N**₂ (0.002 g, 0.0022 mmol) in *ca.* ¹/₂ ml of benzene. The sample was subjected to two freezepump-thaw cycles and D₂ gas (1 atm) was added at 77K on a high-vacuum line. The sample was allowed to warm to ambient temperature, resulting in 4 atm of D₂ gas. After letting sample sit at room temperature for 1 hour a ²H NMR was taken (teal-below). Another ²H NMR was taken after 24 h at room temperature and is shown below in marron.



Figure S46. ²H NMR (C₆H₆, 76.7 MHz) spectrum of **1-N**₂ (2%) and styrene under 4 atm of D₂ after 1 h at room temperature (top). ²H NMR spectrum of **1-N**₂ (2%) and styrene under 4 atm of D₂ of after 24 h at room temperature (bottom). (* denotes ethylbenzene)

A standard J. Young NMR tube was charged with a solution of cyclohexene (11 μ L, 0.112 mmol) and **1-N**₂ (0.002 g, 0.0022 mmol) in *ca*. ¹/₂ ml of benzene-*d*₆. The sample was subjected to two freeze-pump-thaw cycles and D₂ gas (1 atm) was added at 77K on a high-vacuum line. The sample was allowed to warm to ambient temperature, resulting in 4 atm of D₂ gas. After letting sample sit at 60°C for 1 hour a ¹H NMR was taken (below-teal). Another ¹H NMR was taken after 48 h at 60°C and is shown below in maroon.



Figure S47. ¹H NMR (C₆D₆, 500 MHz) spectrum of **1-N**₂ (2%) and cyclohexene under 4 atm of D₂ after 1 h at 60°C (top). ¹H NMR spectrum of **1-N**₂ (2%) and cyclohexene under 4 atm of D₂ of after 48 h at 60°C (bottom).

A standard J. Young NMR tube was charged with a solution of cyclohexene ($12 \mu L$, 0.112 mmol) and **1-N**₂ (0.002 g, 0.0022 mmol) in *ca*. ¹/₂ ml of benzene. The sample was subjected to two freezepump-thaw cycles and D₂ gas (1 atm) was added at 77K on a high-vacuum line. The sample was allowed to warm to ambient temperature, resulting in 4 atm of D₂ gas. After letting sample sit at 60°C for 1 hour a ²H NMR was taken (below-teal). Another ²H NMR was taken after 48 h at 60°C and is shown below in marron.



Figure S48. ¹H NMR (C₆H₆, 76.7 MHz) spectrum of **1-N**₂ (2%) and cyclohexene under 4 atm of D₂ after 1 h at 60°C (top). ²H NMR spectrum of **1-N**₂ (2%) and cyclohexene under 4 atm of D₂ of after 48 h at 60°C (bottom). (* denotes partially deuterated cyclohexane)

Para-hydrogen (p-H₂) Induced Polarization (PHIP) NMR Studies

Sample Preparation. A standard J. Young NMR tube was charged with a solution of styrene (6 μ L, 0.056 mmol) and **1-N**₂ (0.001 g, 0.0011 mmol) in *ca.* $\frac{1}{2}$ ml of benzene. The sample was subjected to two freeze-pump-thaw cycles and *p*-H₂ gas (1 atm) was added at 77K on a high-vacuum line. The sample was kept frozen in liquid nitrogen and warmed to ambient temperature and shaken immediately prior to interesting into the NMR spectrometer. The ALTADENA effect was thus observed. The spectra were collected at 20°C. Increasing the temperature of the probe to 75°C only prolonged the lifetime and intensity of the polarized signals.

NMR Spectrometer. All PHIP NMR data presented herein were collected on a Varian UNITY INOVA 500 NB High-Resolution NMR Console with a 5mm Varian ${}^{1}H{}^{13}C{}^{15}N{}$ PFG Z probe. All spectra were collected in benzene- d_6 and the residual solvent resonance was referenced to 7.16 ppm. ${}^{1}H$ NMR spectra were recorded using 45° pulse angle. The spectral window of 30 ppm was used in both proton and ${}^{1}H$ -OPSY experiments. ${}^{1}H$ -OPSY NMR data was collected via a double quantum coherence pathway using the pulse sequence below (**Figure S47**). The OPSY spectra are anti-phase peaks, and they are generally displayed with absolute mode in the following spectra.^{5,6}



Figure S49: Double quantum OPSY pulse sequence (OPSY-d): the vertical bar at ¹H channel represents $\pi/2$ pulse. Phase cycle: ϕ 1: (y)₄(x)₄, ϕ 2: (x)₄(y)₄, rec: (x)₄(y)₄. Z Gradient: 50 G/cm rectangular gradient was used. First gradient was applied for 1ms in the opposite direction of the second gradient which was applied for 2ms. 0.5ms gradient recovery delays were used after each gradient. The acquisition time was 4 seconds and no delay between scans was used.

Generation of *para***-hydrogen.** A parahydrogen converter was used to generate the *para*-H₂ enriched hydrogen gas. This consisted of copper tubing filled with a hydrous ferric oxide catalyst that was cooled to 15 K using a closed-cycle ⁴He cryostat. A detailed description of the converter can be found in Tom *et al.*⁷, which was able to consistently convert naturally occurring hydrogen gas (3:1 *ortho:para*) to 99.99% *para*-H₂.



Figure S50. ¹H NMR (C₆D₆, 500 MHz, 45° pulse) spectrum of **1-N**₂ (2 mol%) and styrene under 4 atm of p-H₂ at 20°C (top). ¹H-OPSY NMR spectrum of **1-N**₂ (2 mol%) and styrene under 4 atm of p-H₂ at 75°C (bottom).



Figure S51. ¹H NMR (C₆D₆, 500 MHz, 45° pulse) spectrum of **1-N**₂ (2 mol%) and 4-vinylcyclohexene under 4 atm of *p*-H₂ at 20°C (top). ¹H-OPSY NMR spectrum of **1-N**₂ (2 mol%) and 4-vinylcyclohexene under 4 atm of *p*-H₂ at 20°C (bottom).

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