

The Reaction of Cobaloximes with Hydrogen: Products and Thermodynamics

Deven P. Estes, David C. Grills, Jack R. Norton*
Columbia University
Brookhaven National Laboratory

Supporting Information

Table of Contents

Experimental Details	S1
UV-Vis Spectra Under High Pressure	S4
Derivation of Equilibrium Expression	S6
High Pressure NMR Data	S6
Stopped-Flow Reaction of 5b with HNEt ₃ BF ₄	S11
References	S12

Experimental Details

Caution should be used when performing reactions under pressure! All manipulations were performed under an argon atmosphere using standard Schlenk or inert atmosphere box techniques. High pressure NMR spectra were taken using a sapphire NMR tube similar to the design of Owen and Bercaw¹ outfitted with 1/16" o.d. PEEK tubing leading to a pressure gauge and a sealable valve which could be connected to a high pressure manifold, consisting of a hydrogen tank connected to a network of tubing leading to a pressure gauge, a rotary vacuum pump, and the sample tube. After evacuation of the manifold and sample tube, the sample was pressurized with the desired amount of gas and a vortex mixer was used to saturate the solution. This sample tube was then lowered manually into a 300 MHz NMR spectrometer using a custom made shield designed to minimize exposure to the pressurized tube. ***Caution: Working with high gas***

pressures in sapphire tubes is very dangerous. Steps should be taken to minimize exposure to the tube and the manifold. For your safety, the equipment should be regularly tested well above operating pressures. Other NMR spectra were recorded on either a Bruker 300 or 400 MHz instrument.

High Pressure UV-Visible spectra were recorded with a custom-made stainless steel cell equipped with one 2 mm thick sapphire window and one 10 mm thick CaF_2 window (resulting optical path length = 1 cm). This cell was manufactured in the University of Nottingham, Nottingham, UK and was donated to the BNL group by Prof. Michael W. George. It has been described previously (see Fig. 3 in Poliakoff, M. *et al.*, *Angew. Chem. Int. Ed.* **1995**, *34*, 1275-1295). The cell was equipped with a magnetic stir bar and a thermocouple was inserted into one of the ports to allow measurement of the internal cell temperature. The CH_3CN or THF solution was loaded into the cell via a syringe inside an argon glovebox and the cell was sealed. It was then transferred to a high-pressure filling station consisting of a network of 1/16" o.d. stainless steel tubing, high-pressure valves and fittings (Scientific Systems, Inc.), pressure transducers (Omega Engineering, Inc., PX61V1-5KGV), a rotary vacuum pump, and a hydrogen cylinder equipped with a high-pressure regulator. After evacuating all of the tubing and refilling with H_2 several times, the tubing was then filled with H_2 to the desired pressure. The top valve of the high-pressure cell was then opened to saturate the solution with H_2 to the desired pressure. After stirring the solution for several minutes and allowing the pressure to stabilize, the cell was sealed again and taken to an Agilent 8453 diode-array spectrophotometer for acquisition of UV/visible spectra.

Rapid mixing experiments were performed using a HiTech anaerobic stopped flow spectrometer fitted with an Olis rapid scanning monochromator with a 1 cm path length, wavelength range of 300 – 700 nm, a mixing time of less than 3 ms, and 1 ms resolution. Kinetic data were fitted using global analysis.

Spectro–electrochemical reductions were performed using a Pt honeycomb electrode from Pine Instrument Company in a quartz cell with 1.7 mm path length containing either 0.1 M solutions of NBu_4PF_6 in CH_3CN or 0.1 M $\text{NBu}_4[\text{B}(\text{C}_6\text{F}_5)_4]$ in THF referenced to a Ag wire pseudo-reference electrode. The correct potential for reduction was found in a preliminary experiment in which the potential was gradually lowered (100 mV increments) until the desired reduction went to completion.

Benzene and THF were distilled from Na/benzophenone ketyl and stored over 3 Å molecular sieves. Acetonitrile was purified by a previously published procedure.² Deuterated solvents were purified analogously to their protiated counterparts. Complexes **1c**, **2c**, and **5a** were made by known procedures.³ The hydrogen and deuterium gas were purchased as ultra-high purity grade (99.999% pure).

UV-Vis Spectra Under High Pressure

Figure S 1. $\text{Co}(\text{dmgBF}_2)_2(\text{OH}_2)_2$ (1c) in CH_3CN at 70 atm H_2 over 24 hours

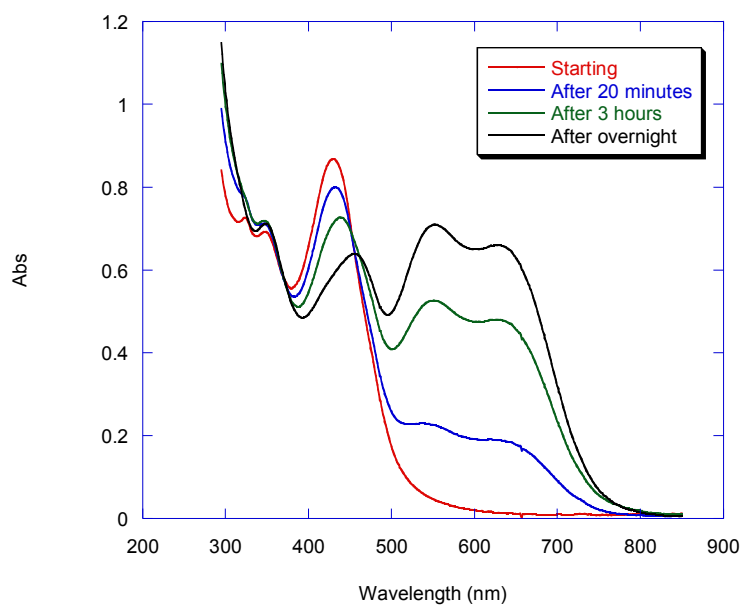


Figure S 2. $\text{Co}(\text{dmgBF}_2)_2(\text{CH}_3\text{CN})_2$ (1a) under variable P_{H_2}

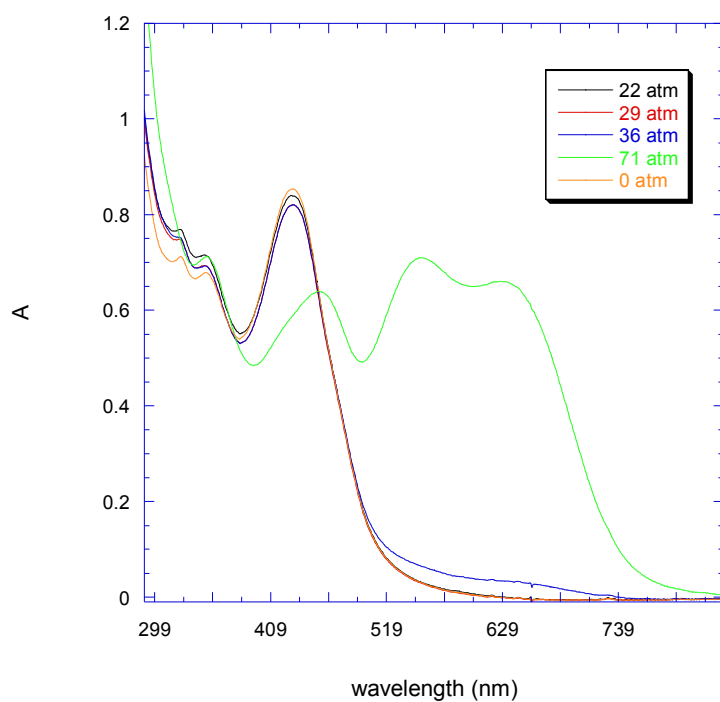


Figure S 3.

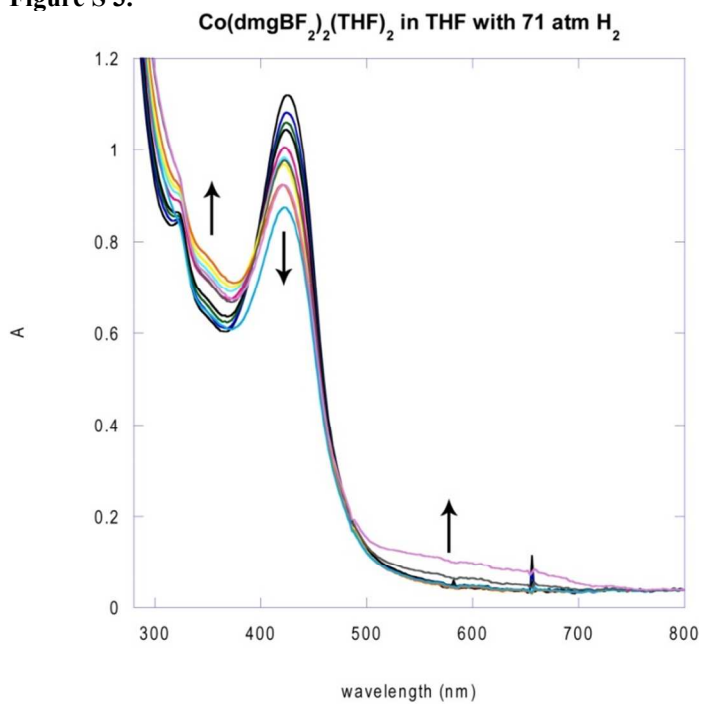
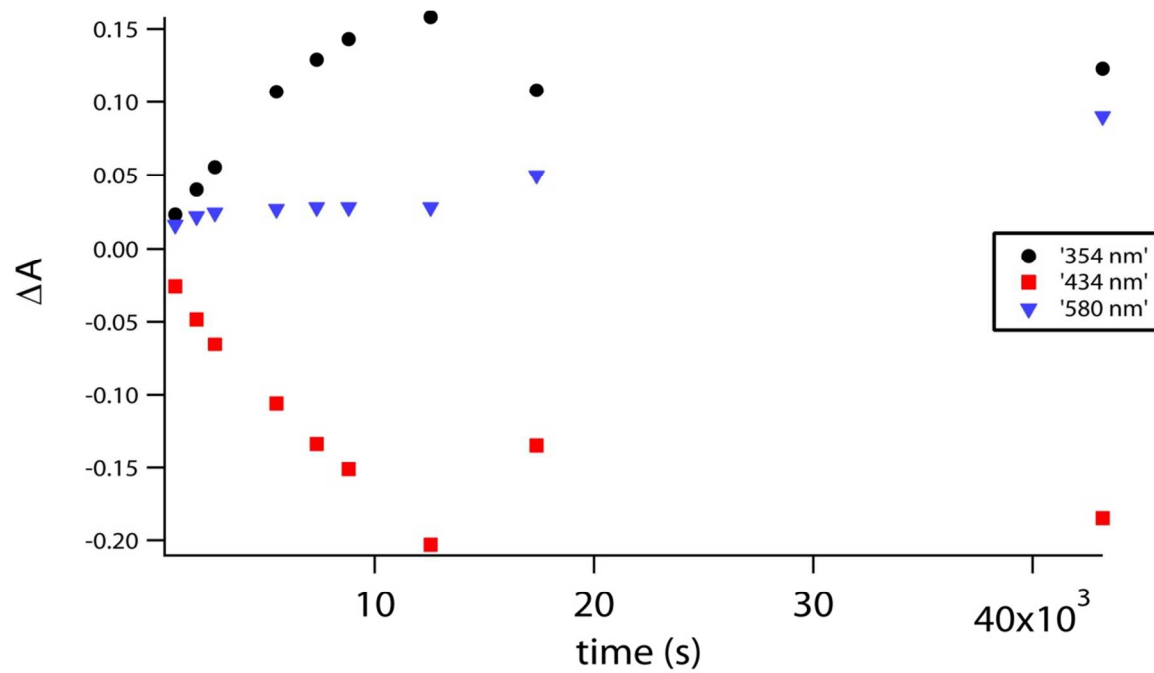


Figure S 4. Plot of absorbances vs time in the hydrogenation of 1b in THF



Derivation of the Equilibrium Expression (eq 6)

$$K_{eq} = \frac{[CoH]^2}{[Co]^2 [H_2]}, \text{ where } [H_2] \gg [Co]_0$$

$$[Co] = [Co]_0 - [CoH] \Rightarrow K_{eq} [H_2] = \left(\frac{[CoH]}{[Co]_0 - [CoH]} \right)^2 \Rightarrow \frac{1}{K_{eq} [H_2]} = \left(\frac{[Co]_0}{[CoH]} - 1 \right)^2$$

$$A_{430} = \epsilon_{Co} [Co] + \epsilon_{CoH} [CoH] = \epsilon_{Co} ([Co]_0 - [CoH]) + \epsilon_{CoH} [CoH]$$

$$[CoH] = \frac{A_{430} - A_{430}^0}{\epsilon_{CoH} - \epsilon_{Co}} \equiv \frac{\Delta}{\Delta\epsilon} \Rightarrow \frac{1}{[H_2]} = K_{eq} \left[\left([Co]_0 \Delta\epsilon \right)^2 \frac{1}{\Delta^2} - 2 \left([Co]_0 \Delta\epsilon \right) \frac{1}{\Delta} + 1 \right]$$

High Pressure NMR Data

H/D Exchange Reactions with complex 2a

Figure S 5. Complex 2a in CD₃CN under 4 atm D₂: ¹H NMR

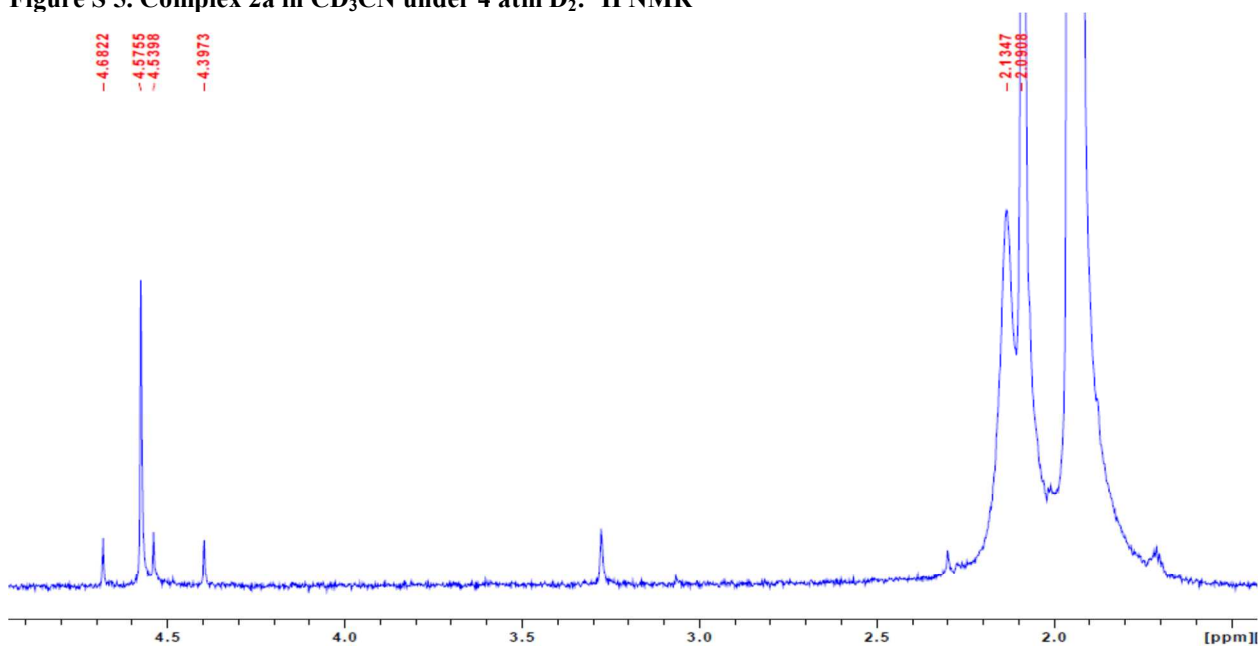


Figure S 6. Complex 2a in CH₃CN under 4 atm D₂: ²H NMR

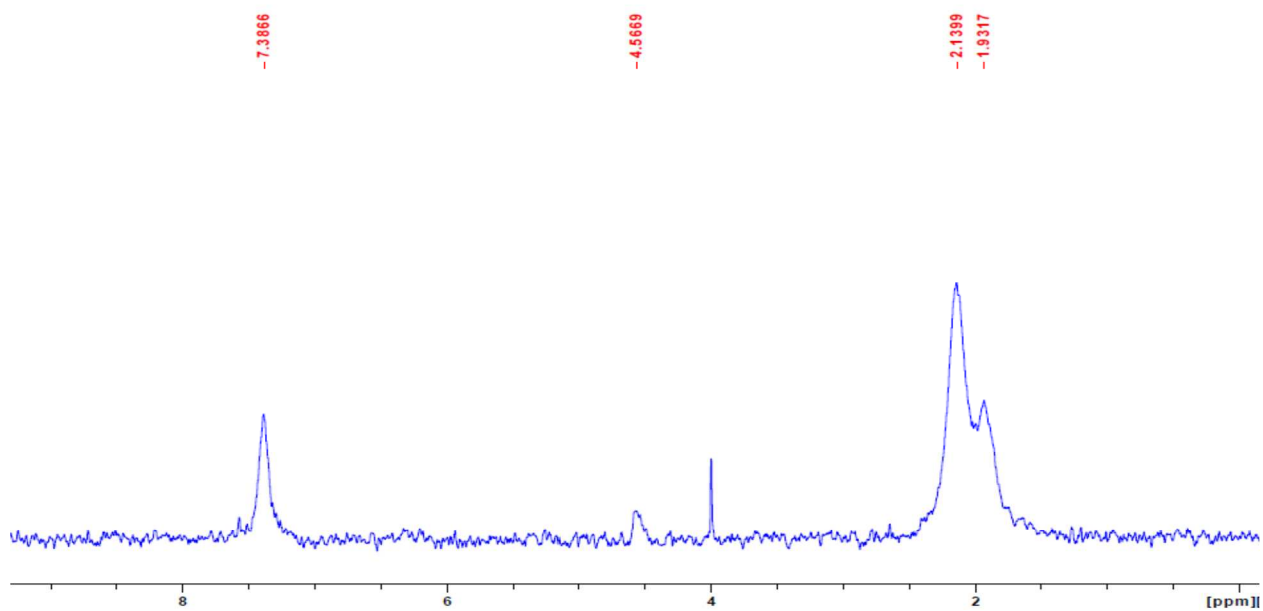


Figure S 7. Complex 1a in CH₃CN after stirring for 24 hours under 5.4 atm D₂: ²H NMR

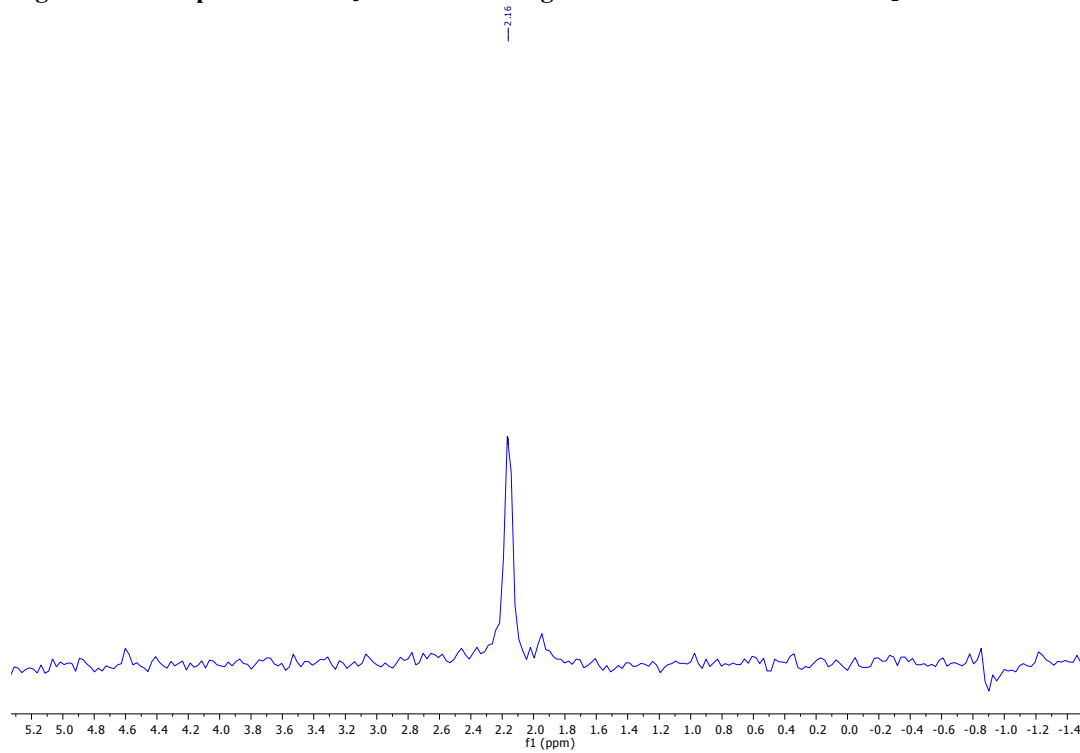
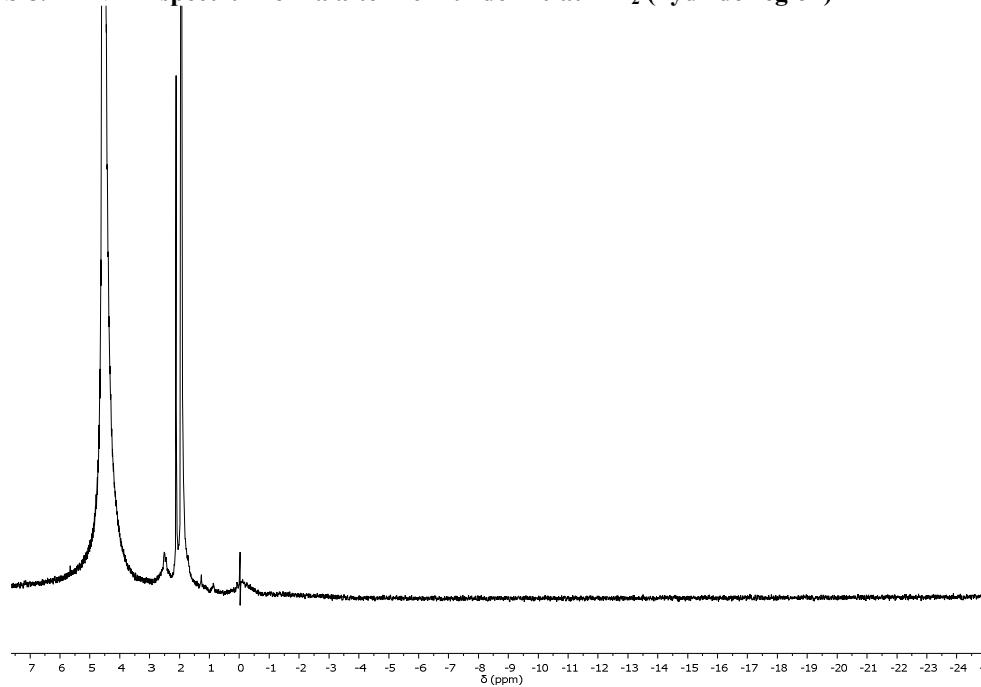


Figure S 8. ^1H NMR spectrum of 1a after 16 h under 70 atm H_2 (hydride region)



*Peaks at 2.08 and ~ 0 ppm are present in the starting spectrum before adding hydrogen (possibly silicone grease broadened by Co)

Figure S 9. Spectrum of 1a in CD_3CN under 70 atm H_2 with 0.02mL of added CD_3OD

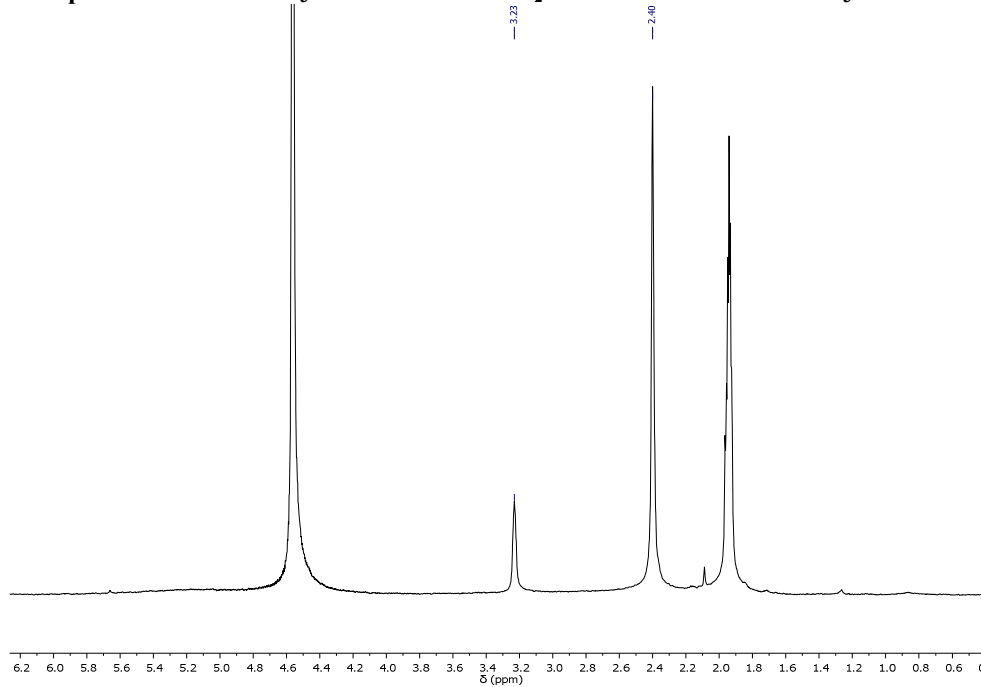
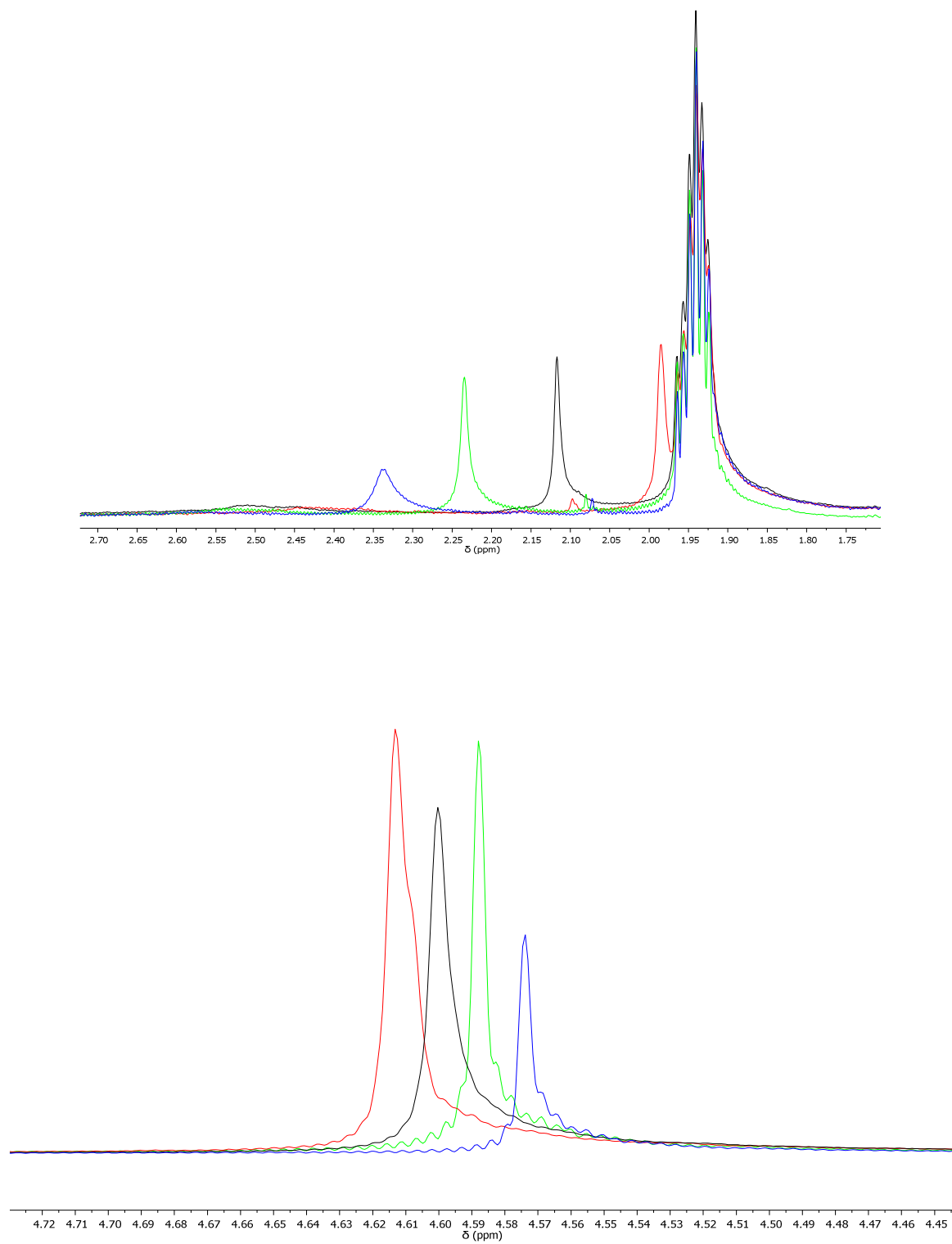
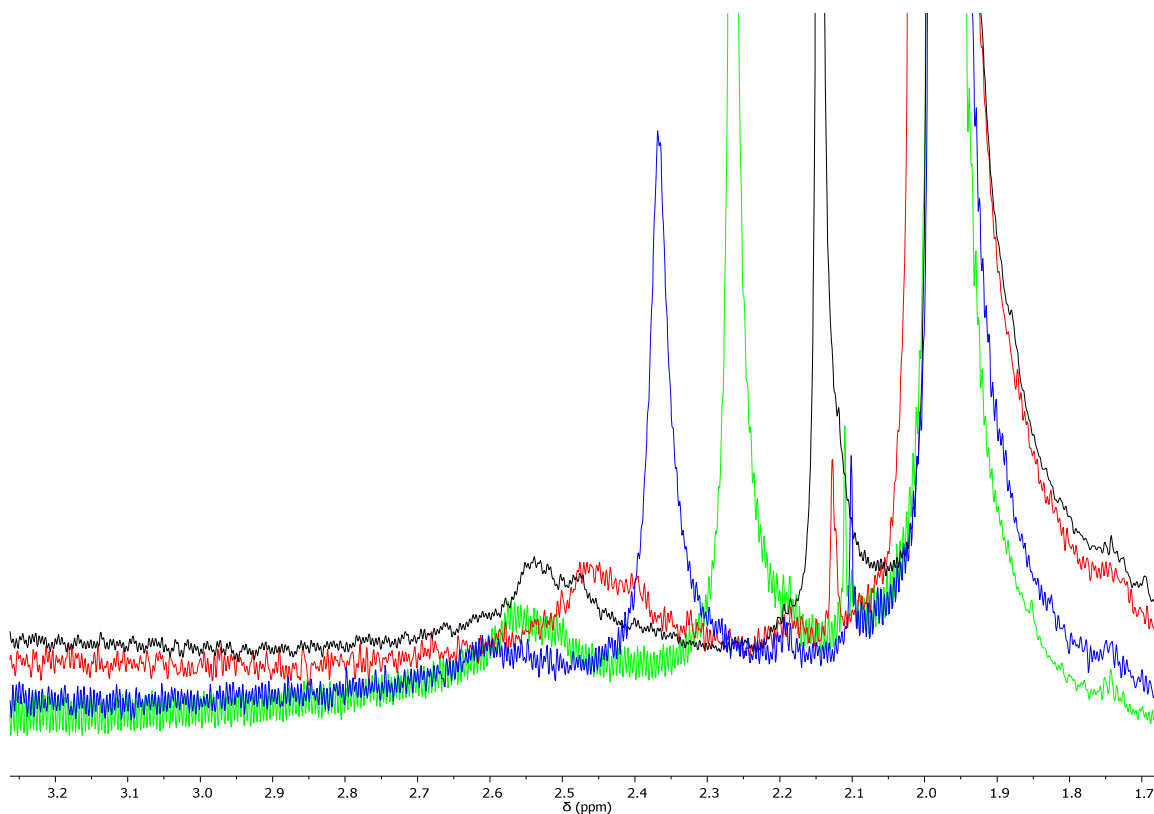


Figure S 10. VT NMR of 1a under H₂ pressure (70 atm at 298 K) (a) CH₃ peak (b) H₂ peak (c) Broad Hydrogen bonded peak





Temperatures: 243 K (blue), 273 K (green), 298 K (black), 333 K (red).

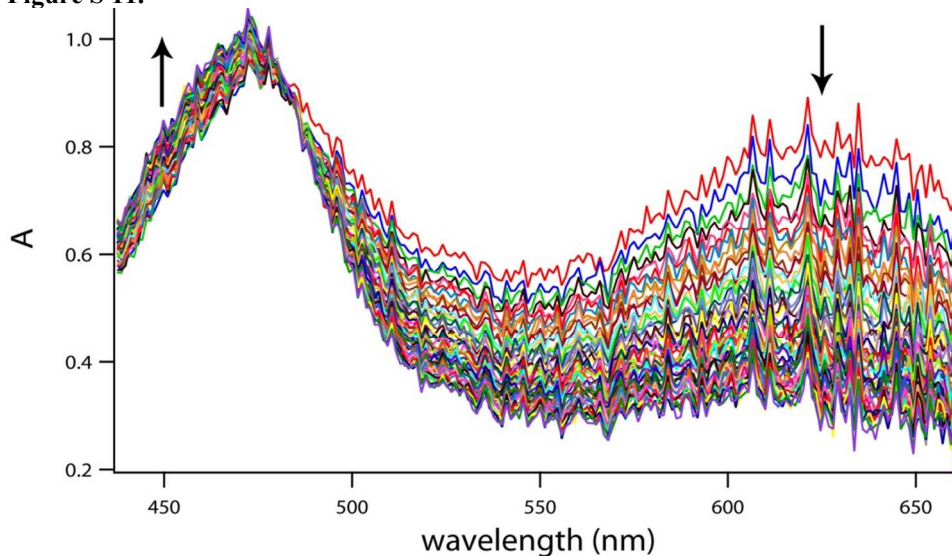
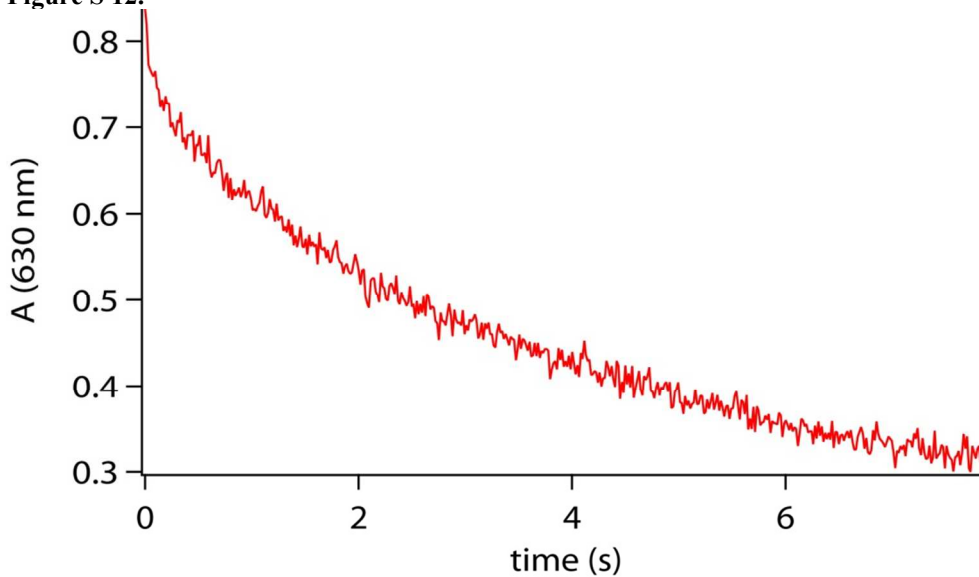
H₂ integrals vs solvent residual signal: 243 K (5.8), 273 K (11.65), 298 K (9.97), 333 K (13.10) show decreasing solubility of H₂ as the temperature is lowered (within ~10% error).

The solubility of hydrogen in acetonitrile as a function of temperature

As the temperature of the NMR tube was lowered from 298 K to 243 K, the internal H₂ pressure also decreased. With an initial pressure of 70 atm at 298 K, we calculated the final pressure to be ~57 atm at 243 K.⁴ It is well-established that the solubility of hydrogen in organic solvents (including acetonitrile) decreases as the temperature is lowered.⁵ Thus, the combination of a drop in H₂ pressure and H₂ solubility as the NMR tube temperature is decreased will result in less dissolved H₂ at the lower temperature. This is consistent with our observed decrease in the intensity of the free H₂ peak at 4.5 ppm as the temperature was lowered.

Stopped-Flow Reaction of **5b with HNEt₃BF₄ in THF:**

A 0.001 M solution of Na[Co(dmgBF₂)₂(THF)] (**5b**) in THF was rapidly mixed with 0.01 – 0.037 M solutions of HNEt₃BF₄ in THF in a stopped-flow spectrometer and monitored over the course of 8 s. These reactions did not result in complete protonation of **5b** over the course of the entire reaction time.

Figure S 11.**Figure S 12.**

References

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