Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting information for:

Platinum-mediated B-H methoxylation of bis(pyrazolyl)borate

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Contents:

1. General Comments:

All manipulations were carried out in 6-dram screw-cap reaction vials under purified N_2 in the glovebox, employing dried, degassed solvents. Syntheses of $[Pt^{II}Ph_2(SMe_2)_2]$[1] and KBp[2] were performed according to literature procedures (see references below). $^1H\{^{11}B\}$, $^{13}C\{^1H\}$, and ^{11}B NMR spectra were recorded on a 400 MHz spectrometer. ^1H, ^{13}C spectra were referenced to the deuterated solvents while ^{11}B NMR spectra were referenced to BF_3-OEt_2 external standard. "Pt-satellites" and "Pt-shoulders" imply resolved and unresolved doublets, respectively, observed as a result of coupling to the ^{195}Pt nucleus. Elemental analyses were performed by analytical services at the Department of Chemistry at the University of British Columbia. ESI-MS (high and low resolution) were compared with isotopic mass envelopes, and the most-intense peaks are reported.

2. Characterization of Potassium bis(pyrazolyl)dihydridoborato diphenylplatinate(II), 1:

1

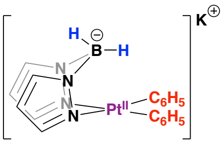


Figure S1. ^1H NMR spectrum of 1 (298 K, 400.2 MHz, CD_3CN, ppm):

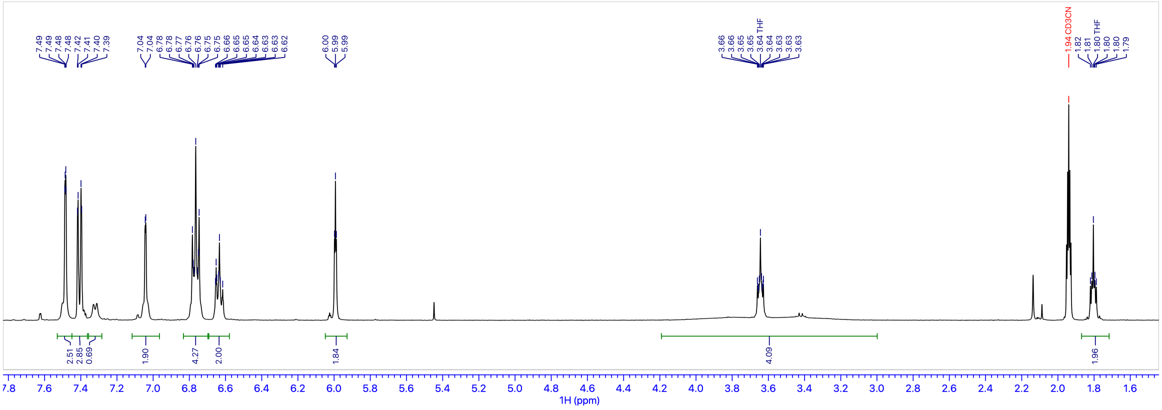


Figure S2. $^{13}C\{^1H\}$ NMR spectrum of 1 (298 K, 100.6 MHz, CD_3CN, ppm):

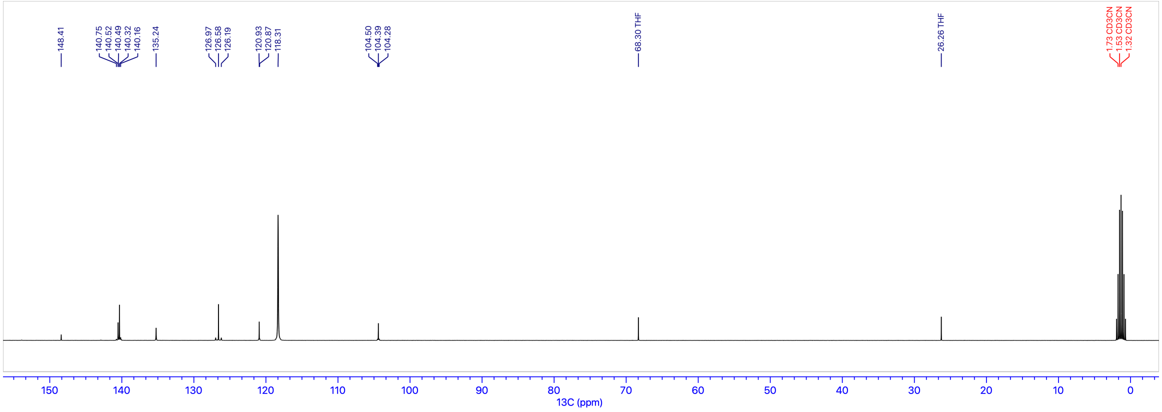
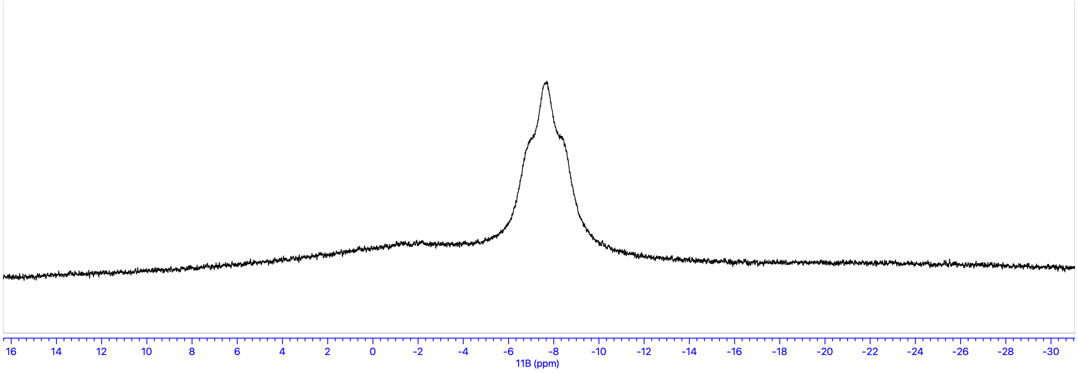


Figure S3. ^{11}B NMR spectrum of 1 (298 K, 128.4 MHz, CD_3CN, ppm):



3. Characterization of Potassium bis(pyrazolyl)dimethoxyborato diphenylplatinate(II), 3:

3

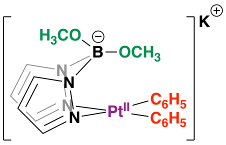


Figure S4. ^{1}H NMR spectrum of 3 (298 K, 400.2 MHz, CD_3CN, ppm):

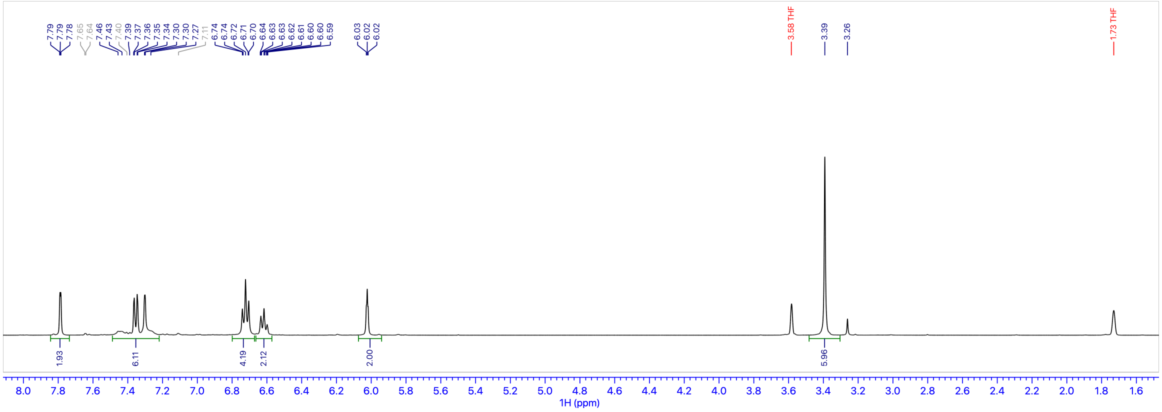


Figure S5. $^{13}C\{^1H\}$ NMR spectrum of 3 (298 K, 100.6 MHz, CD_3CN, ppm):

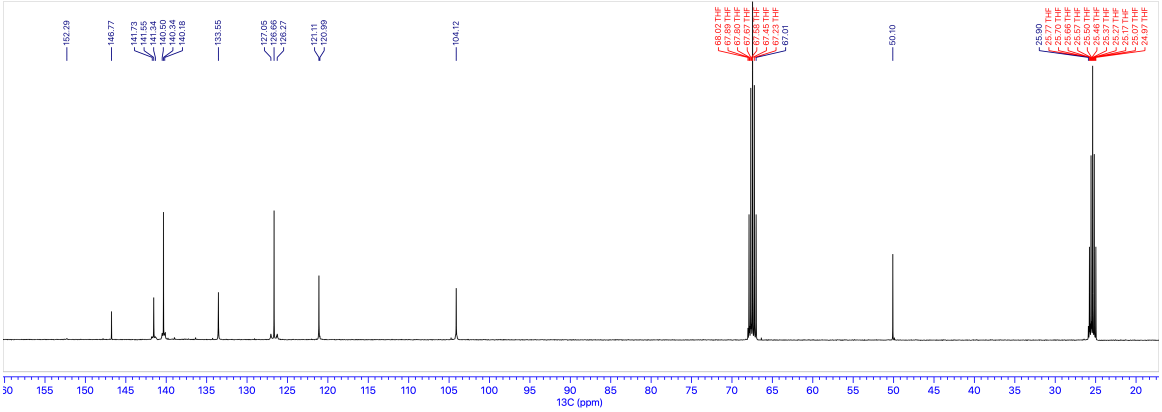
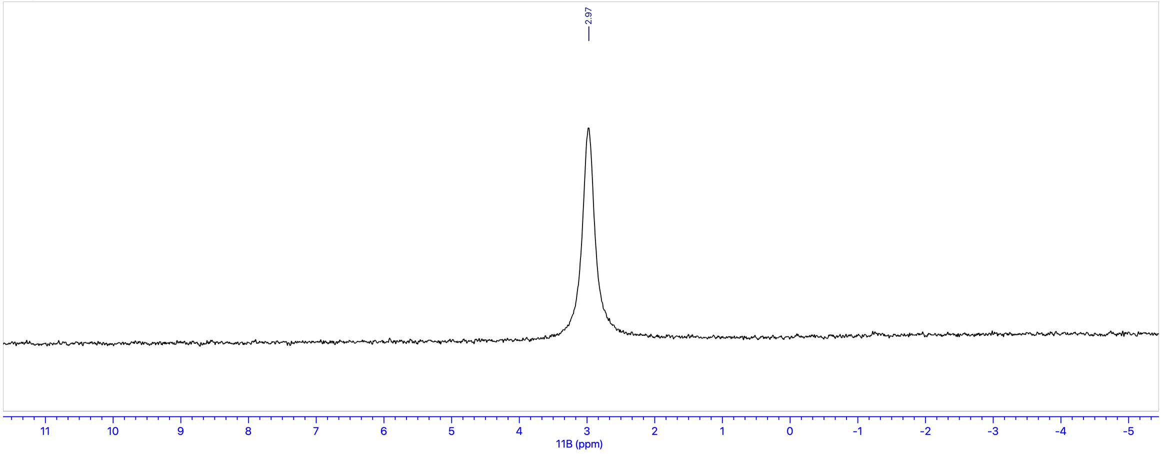


Figure S6.^{11}**B NMR spectrum of 3 (298 K, 128.4 MHz, CD$_3$CN, ppm):**



4. Monitoring conversion of 1 to 2 and finally to 3 by ^{11}B NMR and ESI-MS

10 mg of complex **1** was dissolved in 0.6 mL CH$_3$OH in a vial and the solution was transferred to a Teflon-sealed NMR tube. The NMR tube was placed in the NMR spectrometer pre-heated at 40 °C. The progress of the reaction was monitored by ^{11}B NMR spectroscopy at 1-hour intervals for 20 hours. In a separate experiment, 20 mg of complex **1** was dissolved in 2 mL methanol and stirred in a vial inside the glove-box. 0.2 mL aliquots were drawn at 0 h, 12 h and 48 h, diluted with 0.8 mL methanol and analyzed by ESI-MS.

Figure S7. Stacked plot of ^{11}B NMR spectrum recorded every 1 hour for 20 hours at 40 °C for the reaction of 1 with CH$_3$OH

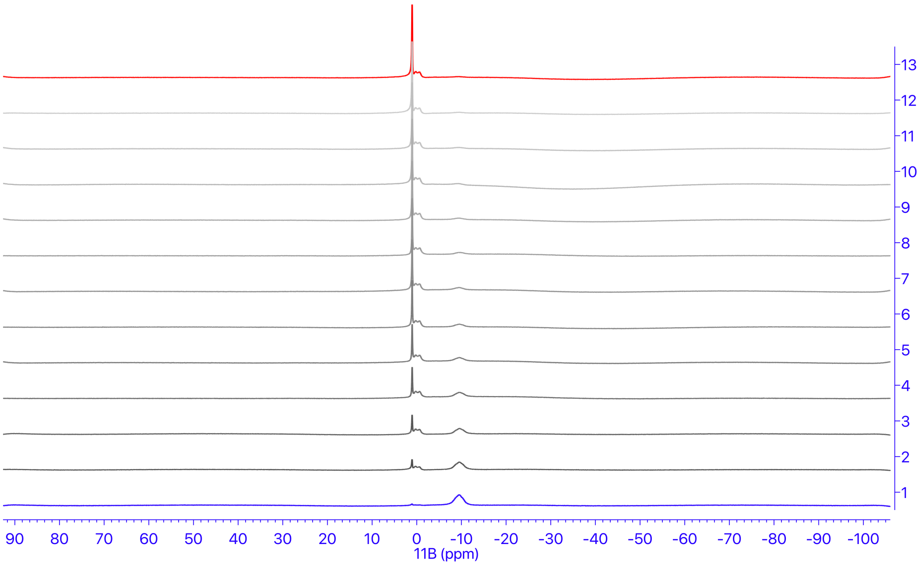
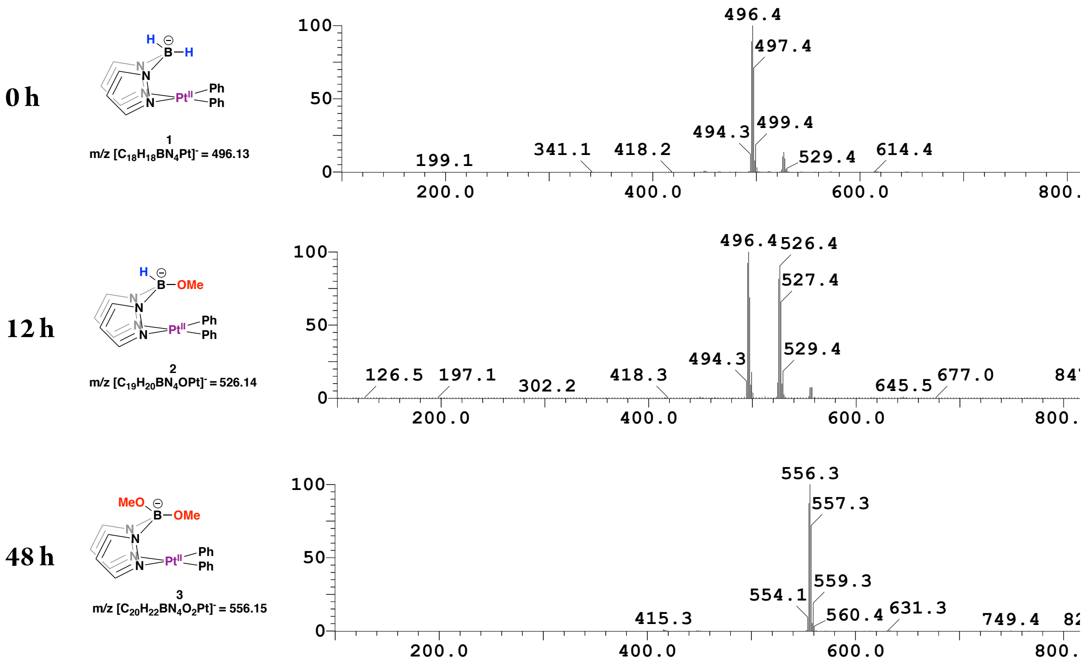


Figure S8. ESI-MS analysis of the reaction of 1 with methanol showing conversion to 2 and 3.



5. Reaction of 1 with CD_3OD as seen by ^1H NMR spectroscopy

10 mg of complex **1** was dissolved in 0.6 mL CD_3OD in a Teflon-sealed NMR tube. The sample was analyzed by ^1H NMR spectroscopy immediately (Fig. S9) and 48 h after dissolution (Fig. S10).

Figure S9. ^1H NMR spectrum of 1 in CD_3OD immediately after dissolution

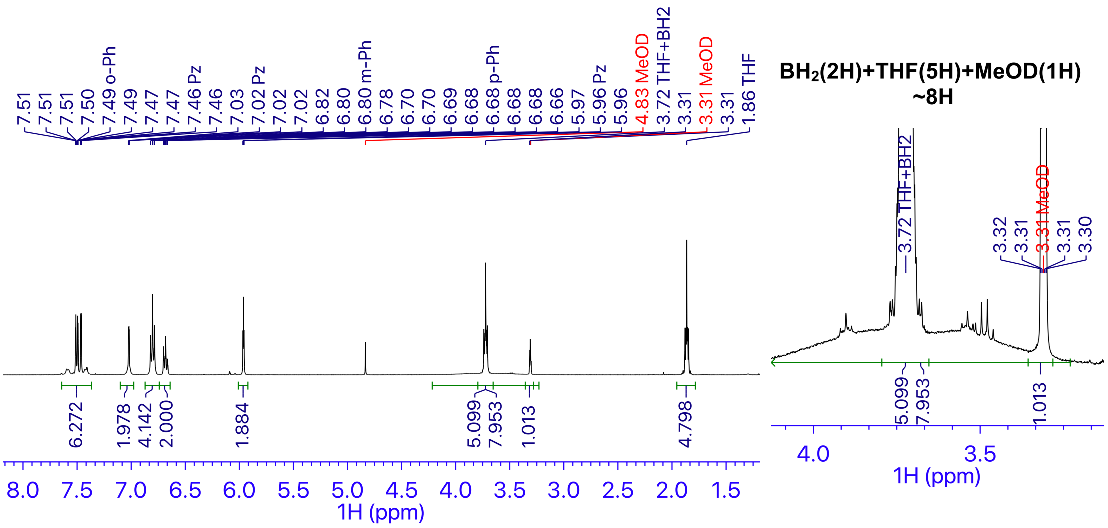
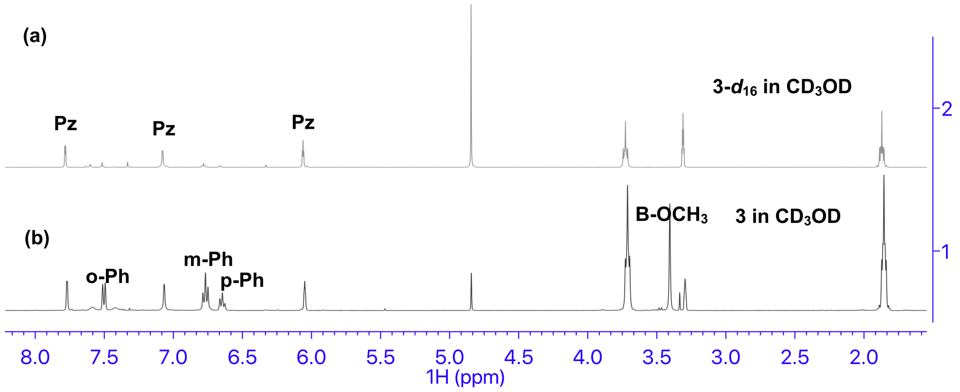


Figure S10. (a) ^{1}H NMR spectrum recorded 48 h after dissolution of 1 in CD_3OD and comparison to the spectrum of 3 in CD_3OD (b).



6. Time-course for the reaction of 1 and 3 with CD_3OD as seen by ^{1}H NMR spectroscopy

10 mg of complex **1** and **3** each were dissolved in 0.6 mL CD_3OD in separate Teflon-sealed NMR tubes and analyzed by ^{1}H NMR spectroscopy at 25 °C for 20 h. The aromatic regions of the spectra were integrated using THF as internal standard. For the reaction of **3**, no deuteration of Pt-C_6H_5 fragments (Fig. S12) nor substitution of B-OCH_3 fragments (Fig. S13) were seen

Figure S11. Time-plot of integration of the aromatic region in the reaction of 1 (blue squares) and 3 (red circles) with CD_3OD

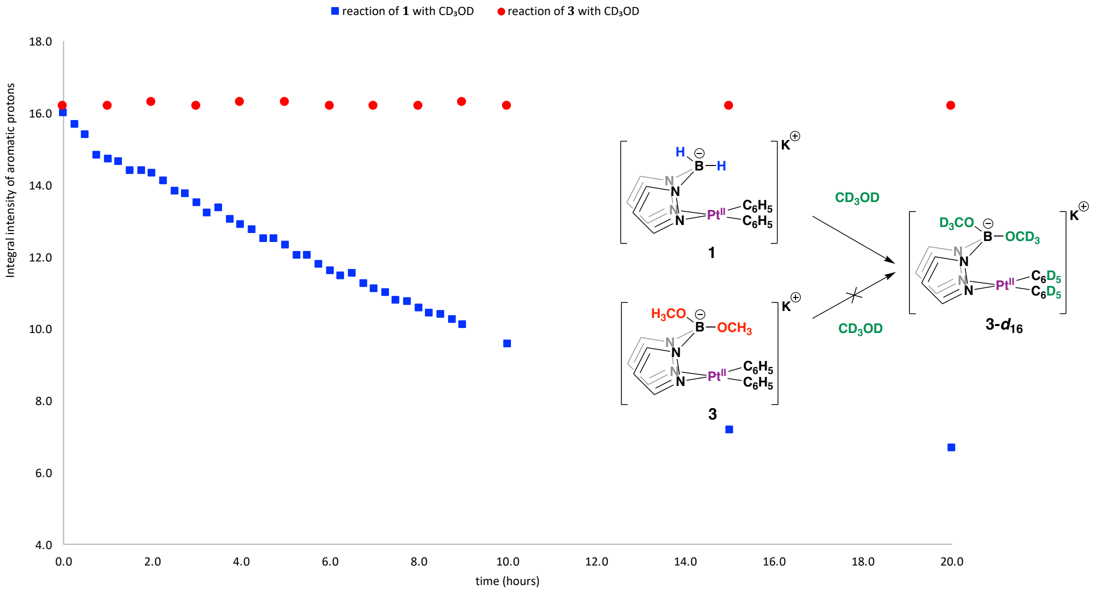


Figure S12. Stacked plot of the aromatic region of the ^{1}H NMR spectra in the attempted reaction of 3 with CD_3OD at 25 °C:

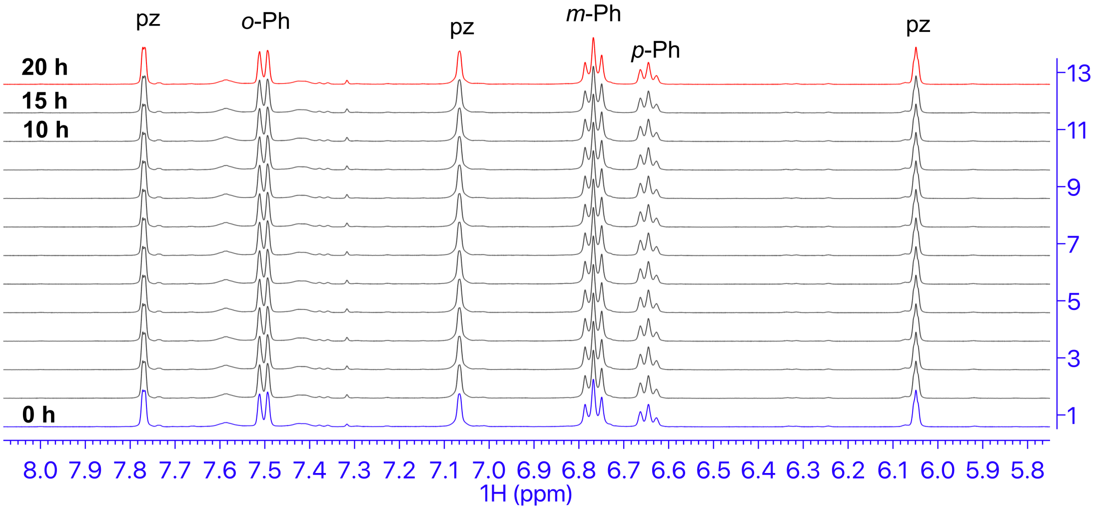
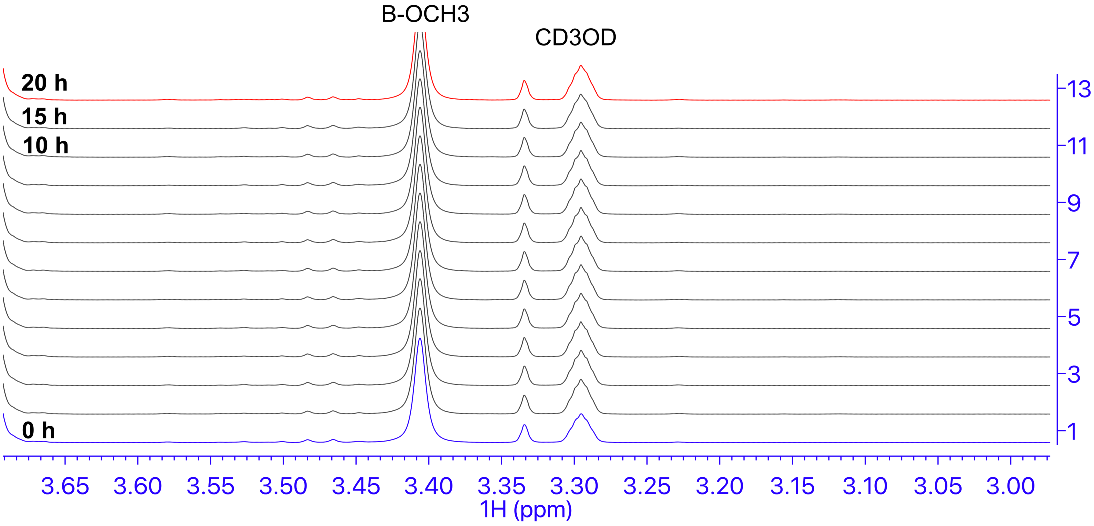


Figure S13. Stacked plot of the methoxy region of the ^{1}H NMR spectra in the attempted reaction of 3 with CD_3OD at 25 °C:



7. Reaction of Potassium bis(pyrazolyl)borohydride with CD_3OD:

15 mg of potassium bis(pyrazolyl)borate (KBp) was dissolved in CD_3OD in a Teflon-sealed NMR tube and analyzed by ^{1}H NMR spectroscopy. The sample was stored for 12 h at 25 °C, during which time, no reaction was found to have occurred (Fig. S14). No H-D was observed in the ^{1}H NMR spectrum. After this time, the NMR tube was immersed in an oil-bath maintained at 50 °C for 12 h. The sample was re-analyzed by ^{1}H NMR

spectroscopy (Fig. S15). H-D was observed as a characteristic triplet at 4.53 ppm ($^1J_{H\text{-}D}$ = 43 Hz). KBp still constituted significant majority of the solution.

Figure S14. ^{1}H NMR spectrum of KBp in CD$_3$OD, immediately after dissolution

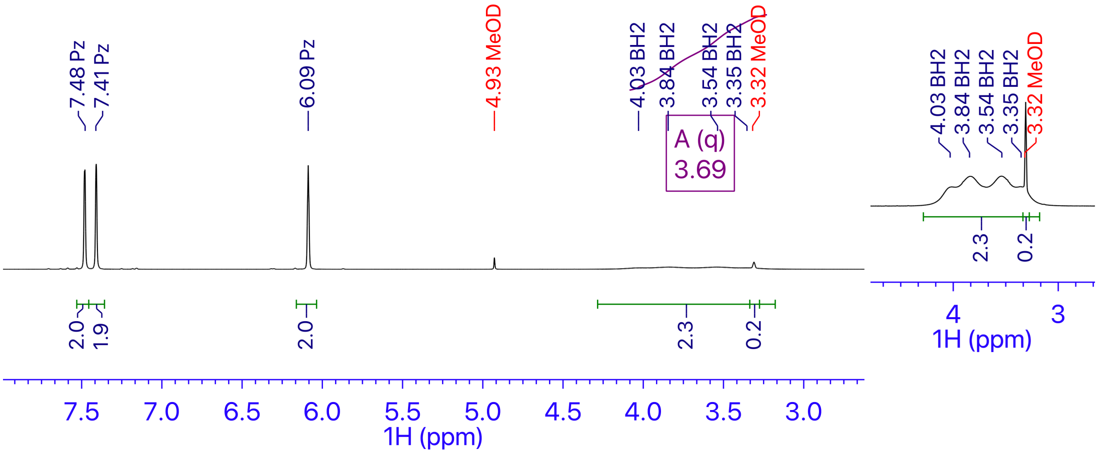
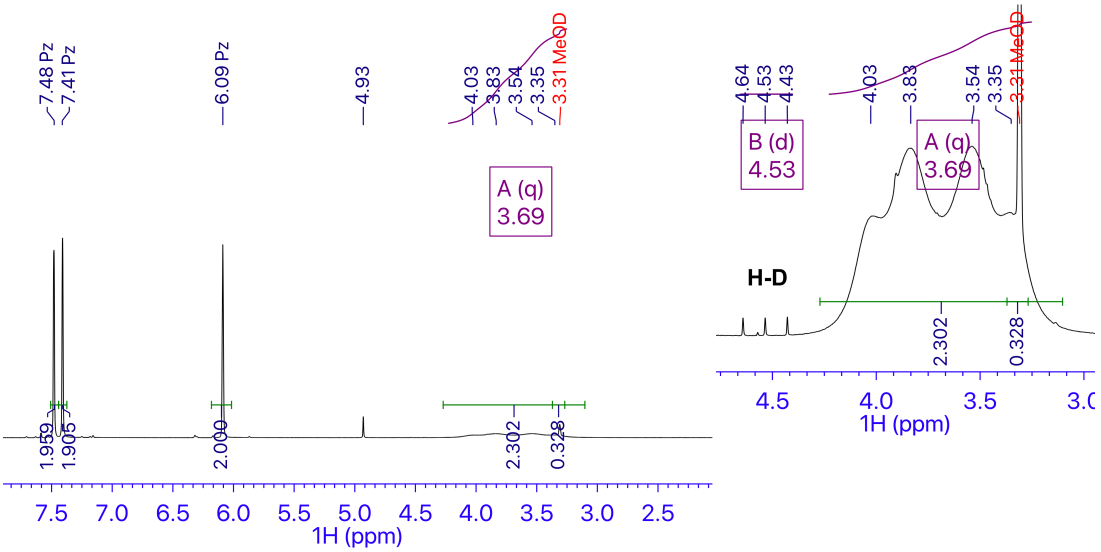


Figure S15. ^{1}H NMR spectrum of KBp in CD$_3$OD after reaction at 50 °C for 12 h (showing H-D).



8. References:

(1) Moret, M.; Chen, P. Interaction of Organoplatinum(II) Complexes with Monovalent Coinage Metal Triflates. *J. Am. Chem. Soc.* **2009**, *131* (15), 5675–5690.

(2) Trofimenko, S.; Long, J. R.; Nappier, T.; Shore, S. G. Poly(1-Pyrazolyl)Borates, Their Transition-Metal Complexes, and Pyrazaboles. In *Inorganic Syntheses: Volume XII*; 2007; Vol. XII, pp 99–109.