

SUPPORTING INFORMATION

Regioselective $^{12}\text{C}/^{13}\text{C}$ CO Exchange Activity of Mixed Valent Fe(II)Fe(I) Model of the H_{ox} State of [FeFe]-Hydrogenase

Christine M. Thomas, Tianbiao Liu, Michael B. Hall, and Marcetta Y. Darensbourg*

Department of Chemistry, Texas A&M University, College Station, TX 77843

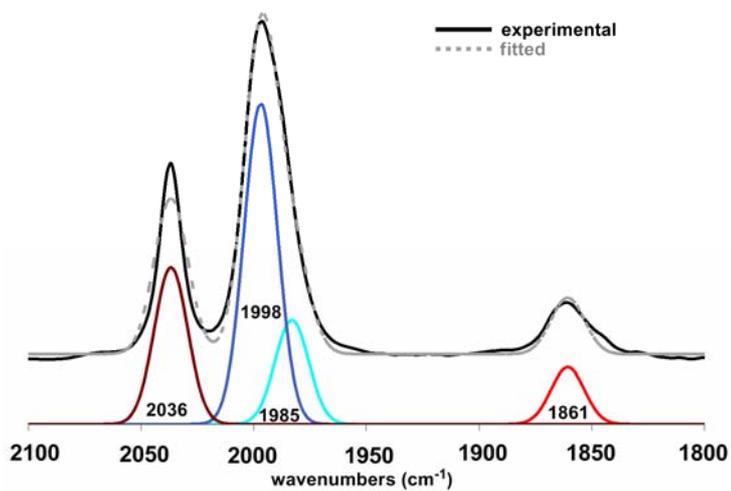
Experimental Procedures

General Considerations. All procedures reported were carried out using standard dry-glove box and Schlenk techniques in the absence of water and dioxygen, unless otherwise noted. Dichloromethane was degassed and dried by sparging with N_2 gas followed by passage through an activated alumina column. Deuterated acetone and ^{13}C were purchased from Cambridge Isotope Laboratories, Inc., and used without further purification. $(\text{PMe}_3)(\text{CO})_2\text{Fe}(\mu\text{-pdt})\text{Fe}(\text{CO})_2(\text{IMes})$ (**1**) was prepared using the procedure reported in the literature.¹ $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ and Cp_2Co were purchased from Aldrich and used without further purification. NMR spectra were recorded on Varian Mercury 300 MHz instruments at ambient temperature. ^1H and ^{13}C NMR chemical shifts were referenced to residual solvent. Infrared spectra were recorded on a Bruker Tensor 27 instrument using a 0.1 mm CaF cell.

Standard Procedure ^{13}C CO Exchange Experiments. $[(\text{PMe}_3)(\text{CO})_2\text{Fe}(\mu\text{-pdt})\text{Fe}(\text{CO})_2(\text{IMes})][\text{PF}_6]$ (**1**⁺) was prepared in situ at $-78\text{ }^\circ\text{C}$ via addition of a solution of $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ (0.015 g, 0.045 mmol) in CH_2Cl_2 (5 mL) to a stirring solution of **1** (0.032 g, 0.045 mmol) in CH_2Cl_2 (10 mL) in a dry ice/acetone bath. After stirring for 15 minutes at $-78\text{ }^\circ\text{C}$, the resulting brown solution was frozen with liquid N_2 . The headspace above this frozen solution was evacuated, then back-filled with ^{13}C . The reaction mixture was then allowed to thaw and warm to $-78\text{ }^\circ\text{C}$, and ^{13}C CO exchange progress was monitored via IR spectroscopy of aliquots of this solution.

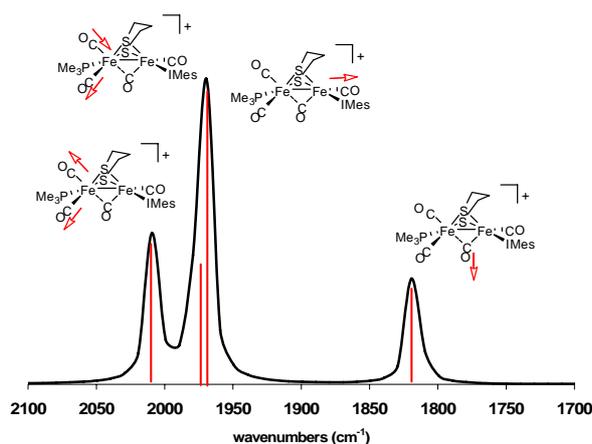
Standard Procedure for Cp_2Co Reduction Experiments. ^{13}C CO was removed from the reaction vessel via brief exposure of the solution to vacuum while maintaining the temperature at $-78\text{ }^\circ\text{C}$. Under N_2 , a pre-cooled solution of Cp_2Co (0.009 g, 0.05 mmol) in CH_2Cl_2 (5 mL) was added to the reaction mixture. After 15 minutes, the solution was allowed to warm to room temperature and solvent was removed in vacuo. The resulting red solids were extracted with 1:1 toluene/hexanes and filtered through a plug of silica gel. Solvent was removed and ^{13}C NMR (75 MHz, acetone- d_6) spectra were recorded on the resulting solid without further purification.

¹ Liu, T.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2007**, *129*, 7008-7009.



Deconvoluted Infrared Spectrum of 1^+ . IR spectrum of 1^+ (in CH_2Cl_2 solution) was deconvoluted using PeakFit 4.12. Figure above shows the experimental IR spectrum of 1^+ (solid, black), the four component bands (solid, multicolored), and the resulting fitted spectrum (dotted, gray).

DFT Vibrational Frequency Calculation of 1⁺. Geometry optimization and analytical frequency calculation were performed using a hybrid functional - the three parameter exchange functional of Becke (B3)² and the correlation functional of Lee, Yang, and Parr (LYP),³ B3LYP – as implemented in Gaussian 03. The effective core potentials and associated basis set of Hay and Wadt (LANL2DZ) were used on the iron, sulfur, and phosphorus atoms.⁴ For iron, the two outermost p functions were replaced by the reoptimized 4p functions as suggested by Couty and Hall.⁵ For sulfur and phosphorus, the basis set was augmented by the d polarization function of Höllwarth et al.⁶ All carbon, nitrogen, oxygen and hydrogen atoms were represented using Dunning's double zeta valence basis (D95).⁷



Although the absolute numbers for the Fe-CO vibrations are not accurate, the general pattern and intensities match well with the experimental IR spectrum and allow the assignment of the IR bands as shown in the figure above.

² Becke, A. D.; *J. Chem. Phys.* **1993**, *98*, 5648-5652.

³ Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *37*, 785-789.

⁴ (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284-398. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270-283.

⁵ Couty, M.; Hall, M. B. *J. Comp. Chem.* **1996**, *17*, 1359-1370.

⁶ Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237-240.

⁷ (a) Dunning, T. H., Jr.; Hay, P. J., in: Schaefer, H. F., III (Ed.), *Methods of Electronic Structure Theory*, vol. 3, Plenum Press, 1977. (b) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823-2833.

Reversibility of $^{13}\text{CO}/^{12}\text{CO}$ Exchange.

To confirm the reversibility of the CO ligand exchange process, a fully ^{13}CO -labeled solution of $\mathbf{1}^+$ in CH_2Cl_2 at $-78\text{ }^\circ\text{C}$ (generated by briefly warming a solution of $\mathbf{1}^+$ to room temperature under ^{13}CO) was exposed to 1 atm ^{12}CO and allowed to warm to room temperature. After 30 minutes at room temperature, the IR revealed that the unlabeled starting material $\mathbf{1}^+$ had been regenerated. A small amount of neutral $\mathbf{1}^+$ (unlabeled) was also formed as a result of the temperatures required to achieve complex exchange.

