Eur. J. Inorg. Chem. **2010** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2011 · ISSN 1434–1948

SUPPORTING INFORMATION

DOI: 10.1002/ejic.201001037
Title: Favorable Protonation of the (μ-edt)[$Fe_2(PMe_3)_4(CO)_2$(H-terminal)]$^+$ Hydrogenase Model Complex Over Its Bridging μ-H Counterpart: A Spectroscopic and DFT Study
Author(s): Mary Grace I. Galinato, C. Matthew Whaley, Dean Roberts, Peng Wang, Nicolai Lehnert*

Figure S1. DFT (BP86/TZVP) predicted Raman spectrum of the bridging hydride isomer (μ-H) of (μ-edt)$[Fe_2(PMe_3)_4(CO)_2H]^+$.

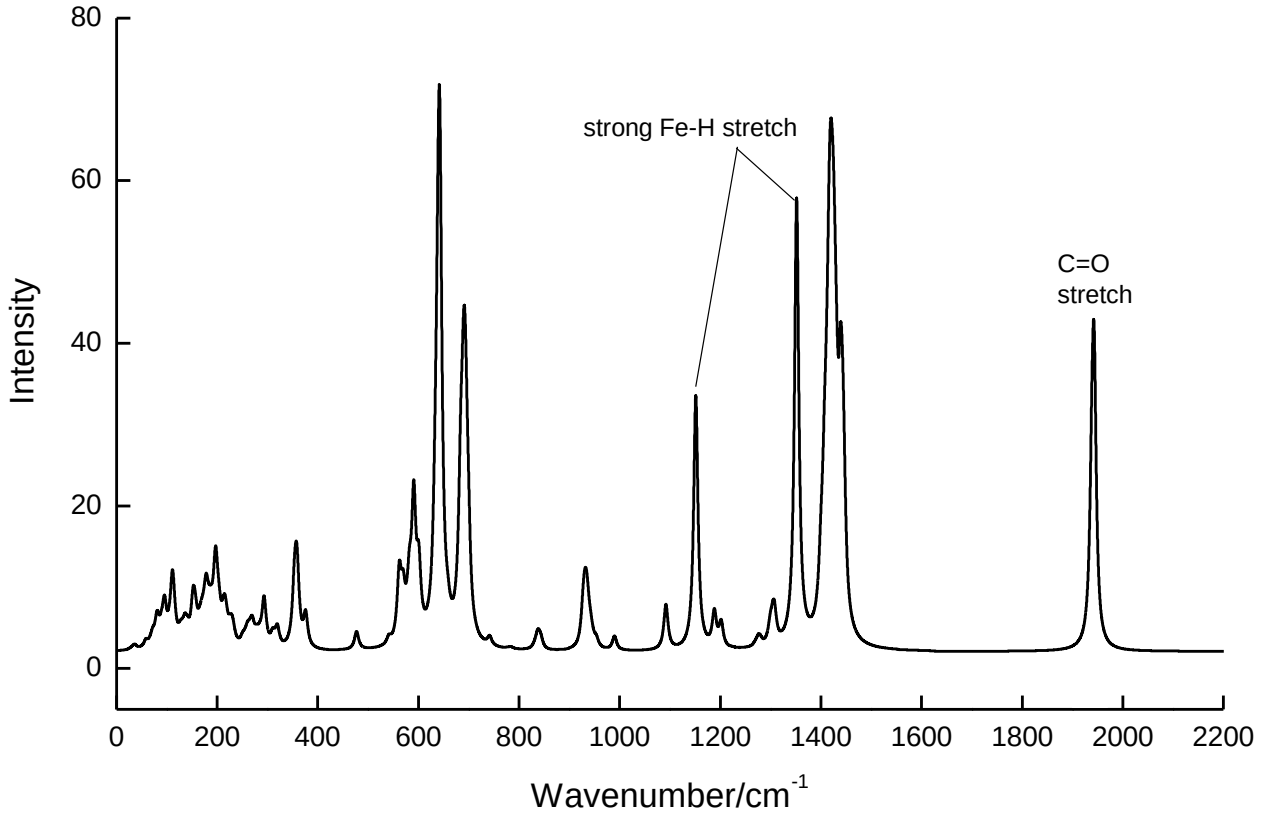


Figure S2. FT-Raman spectrum of solid *D*-term (μ-edt)$[Fe_2(PMe_3)_4(CO)_2D]^+$. An excitation wavelength of 1064 nm was used.

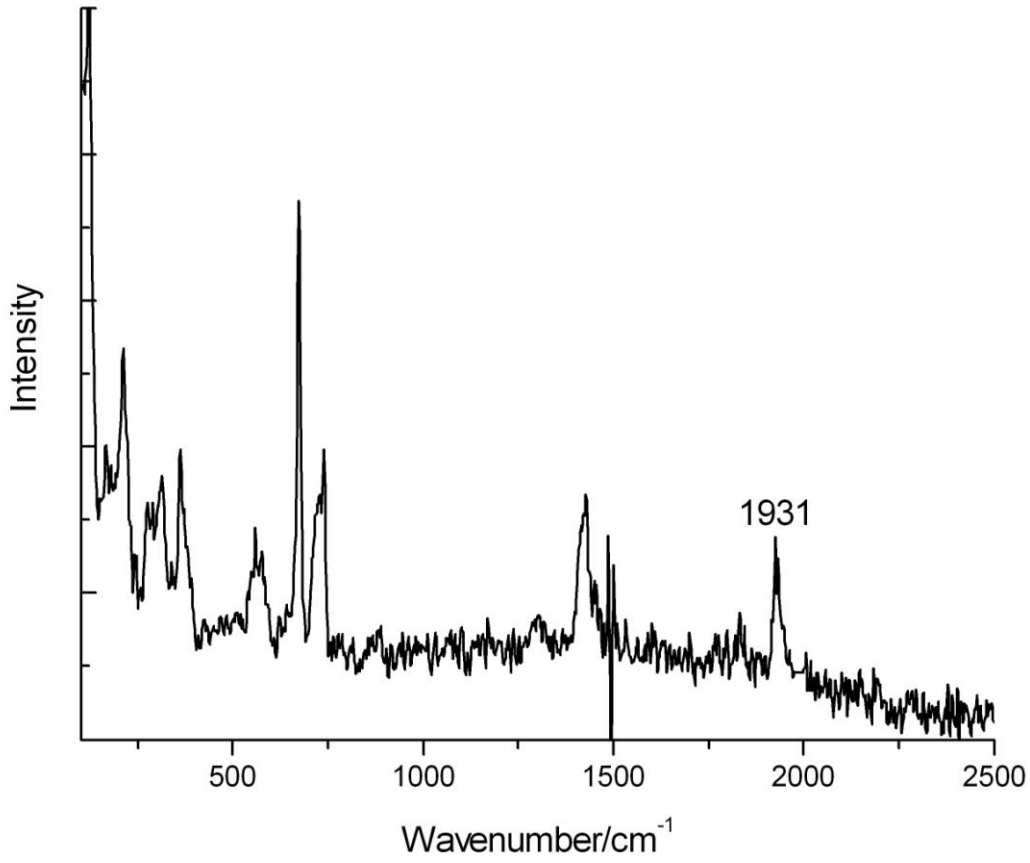


Figure S3. DFT (BP86/TZVP) predicted Raman spectrum of the *H*-terminal isomer (*H*-term) of (μ-edt)$[Fe_2(PMe_3)_4(CO)_2H]^+$. Curiously, the intensity of the Fe-H stretch is largely overestimated in the calculations.

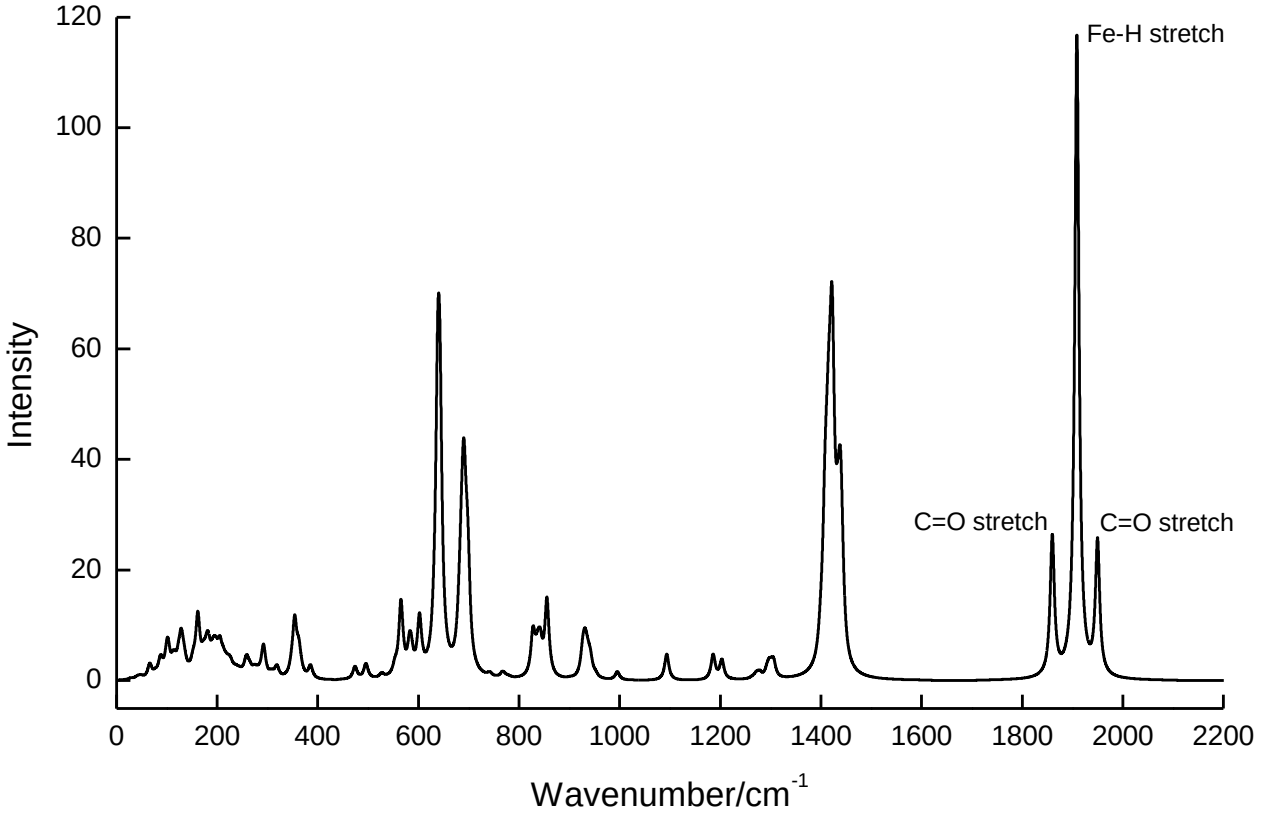


Figure S4. FT-IR spectra of *H*-term and *D*-term (μ-edt)[$Fe_2(PMe_3)_4(CO)_2$ H/D]$^+$. Note that the ν(C=O) stretching mode in *D*-term (emphasized by the bold line) is slightly shifted to lower energy and has a greater relative intensity, indicating the presence of a fraction of the μ-D isomer.

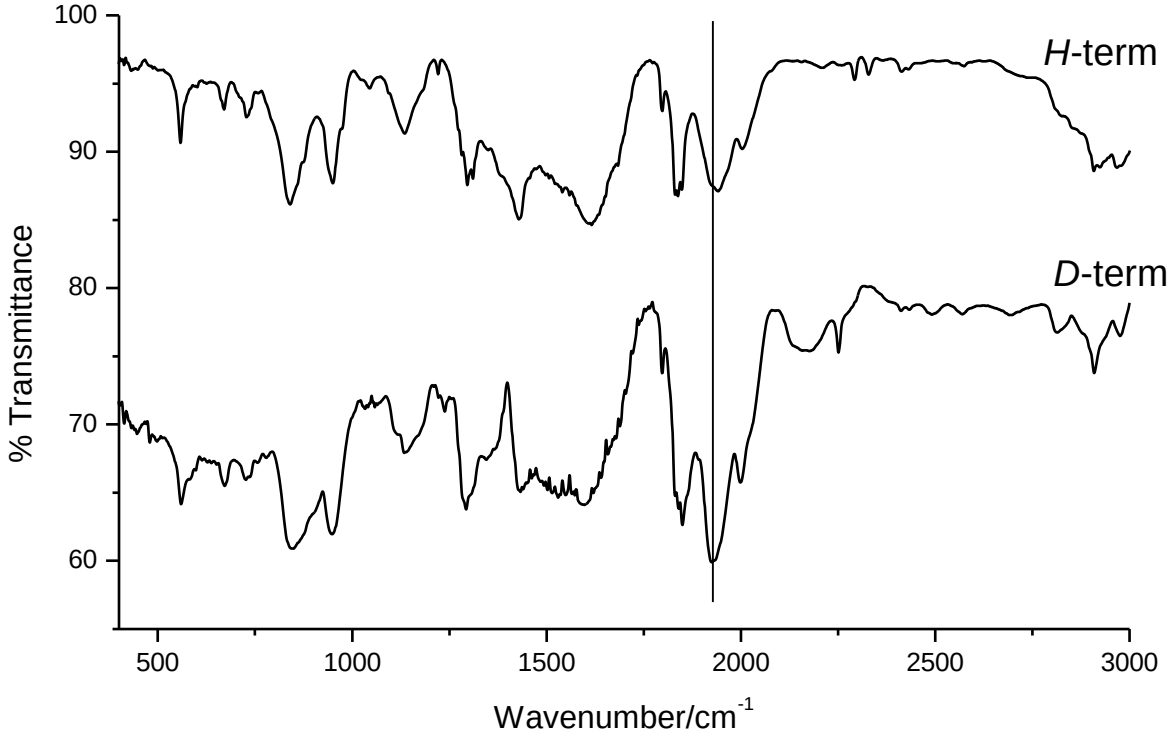


Figure S5. DFT (BP86/TZVP) predicted structure of the dihydrogen complex of *H*-term, (μ-edt)$[Fe_2(PMe_3)_4(CO)_2\,H_2]^{2+}$, in the absence of base. The calculated Fe-H_2 distance is 1.80 Å.

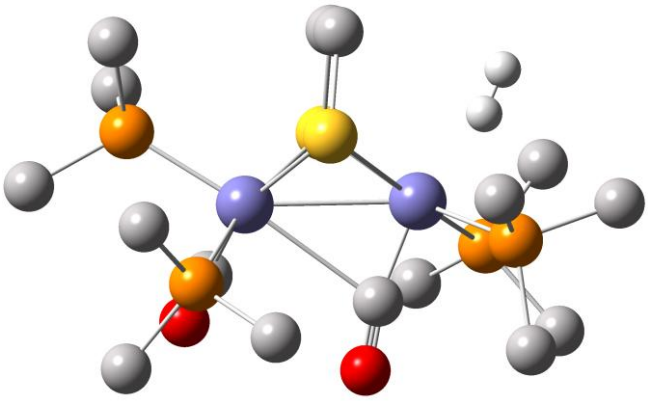
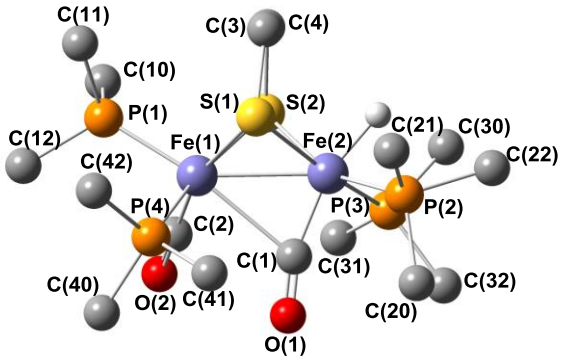


Figure S6. Optimized structures of the *H*-term (top) and μ-H (bottom) isomers of (μ-edt)$[Fe_2(PMe_3)_4(CO)_2H]^+$ using BP86/TZVP (colored version). The atomic labeling scheme is used in pertinent sections of the discussion. Hydrogen atoms of organic side chains are omitted for clarity.



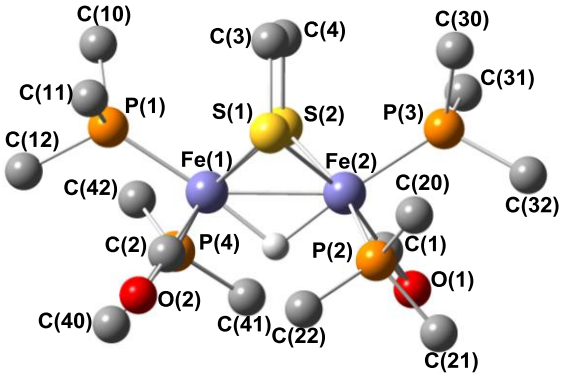
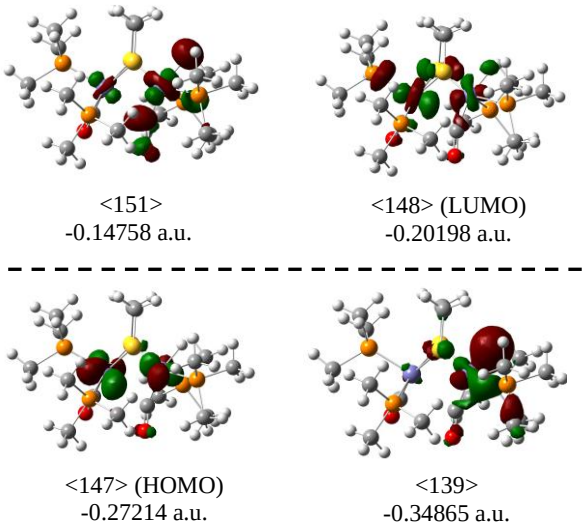


Figure S7. Contour plots of selected MOs of *H*-term (μ-edt)[$Fe_2(PMe_3)_4(CO)_2H$]$^+$ calculated with BP86/TZVP (colored version).



<151>
-0.14758 a.u.

<148> (LUMO)
-0.20198 a.u.

<147> (HOMO)
-0.27214 a.u.

<139>
-0.34865 a.u.

Figure S8. Contour plots of selected MOs of μ-H (μ-edt)[$Fe_2(PMe_3)_4(CO)_2H]^+$ calculated with BP86/TZVP (colored version).