

Spectroscopic and Electrochemical Characterization of Four Stable Protonation States in a Novel Iron Hydrogenase Active Site Mimic

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A novel iron hydrogenase active site mimic, **1** ($[\text{Fe}_2(\mu\text{-adt})(\text{CO})_4(\text{PMe}_3)_2]$, adt = azadithiolate), has been synthesized and the spectroscopic and electrochemical properties of four different protonation states have been investigated. The combination of the adt bridge and electron donating phosphine ligands allows for protonation of the adt nitrogen ($[\text{Fe}_2(\mu\text{-Hadt})(\text{CO})_4(\text{PMe}_3)_2]^+$, $[\mathbf{1H}]^+$), the Fe-Fe bond ($[\text{Fe}_2(\mu\text{-adt})(\mu\text{-H})(\text{CO})_4(\text{PMe}_3)_2]^+$, $[\mathbf{1Hy}]^+$) or both sites simultaneously ($[\text{Fe}_2(\mu\text{-Hadt})(\mu\text{-H})(\text{CO})_4(\text{PMe}_3)_2]^{2+}$, $[\mathbf{1HHy}]^{2+}$). Selective formation of either $[\mathbf{1H}]^+$ or $[\mathbf{1Hy}]^+$ relies on the remarkably slow formation of the hydride ($k \approx 10^{-2} \text{ M}^{-1}\text{s}^{-1}$). IR spectra of **1** and the protonated analogues show the expected average shift of the carbonyl frequencies of ~ 16 , ~ 80 , and 96 cm^{-1} for $[\mathbf{1H}]^+$, $[\mathbf{1Hy}]^+$, and $[\mathbf{1HHy}]^{2+}$, respectively. ^1H - and ^{31}P -NMR spectra confirm the assignment of the IR spectra and reveal the bridging nature of the hydride ligand. Electrochemically, **1** undergoes irreversible reduction at **-2.18 V** vs ferrocene and upon protonation the potential shifts to **-1.57**, **-1.11** and **-1.00 V** for $[\mathbf{1H}]^+$, $[\mathbf{1Hy}]^+$, and $[\mathbf{1HHy}]^{2+}$, respectively.

