

## Supplementary Material

### Protonation of the N<sub>2</sub>-reduction catalyst [HIPTN<sub>3</sub>N]Mo(III) investigated by ENDOR spectroscopy

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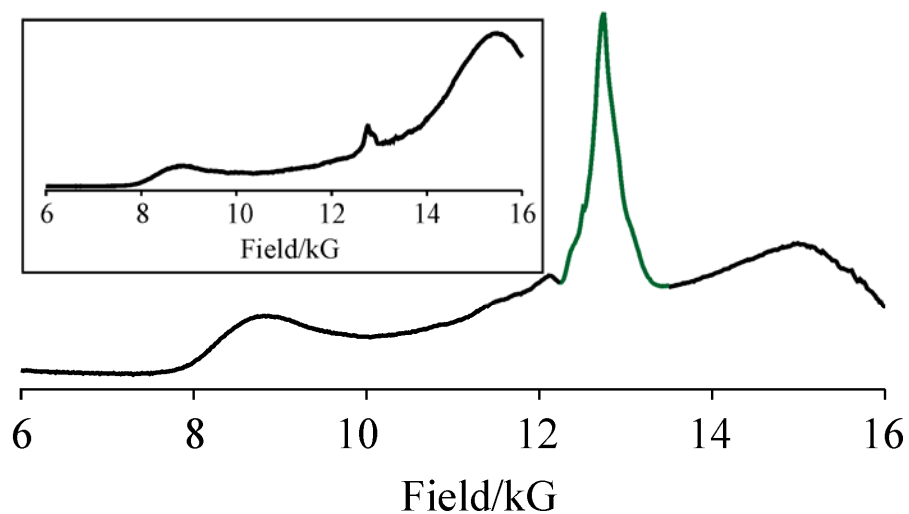
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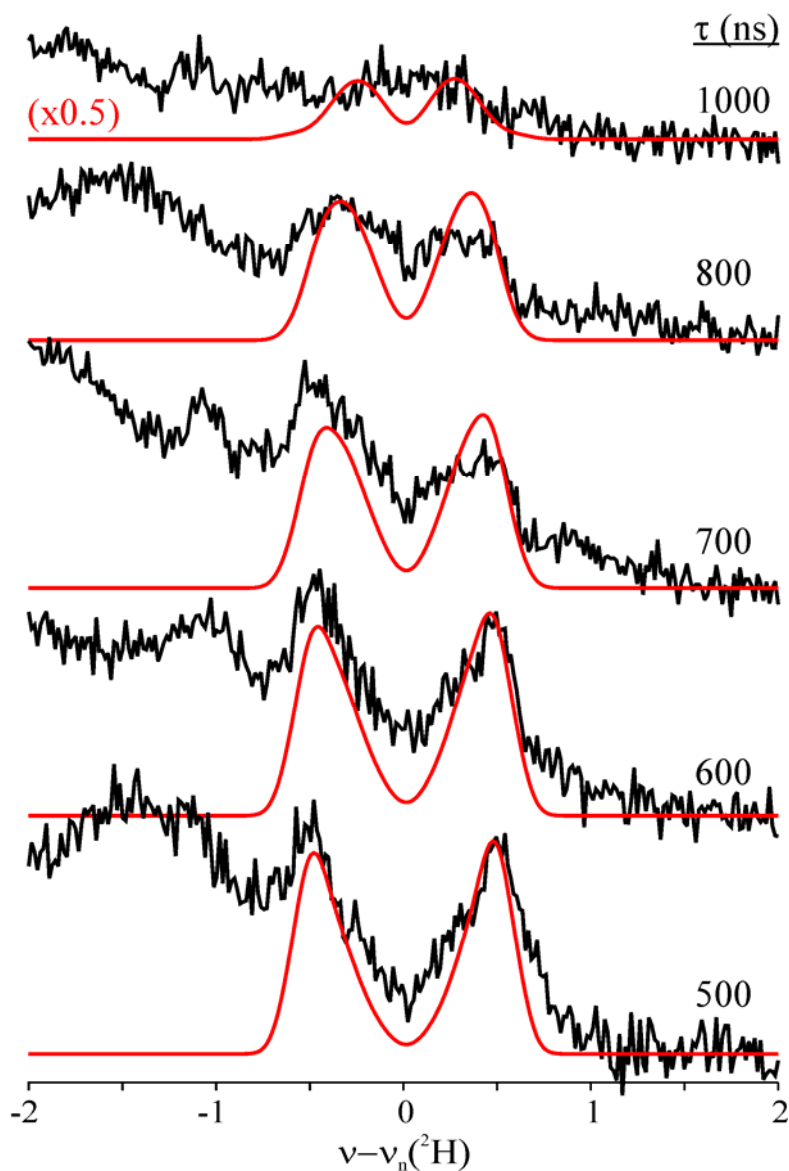
**Figure S3.** Complete 2D field-frequency pattern of Mims ENDOR spectra from <sup>2</sup>HMoCO<sup>+</sup>, with ENDOR simulations.

**Figure S1**



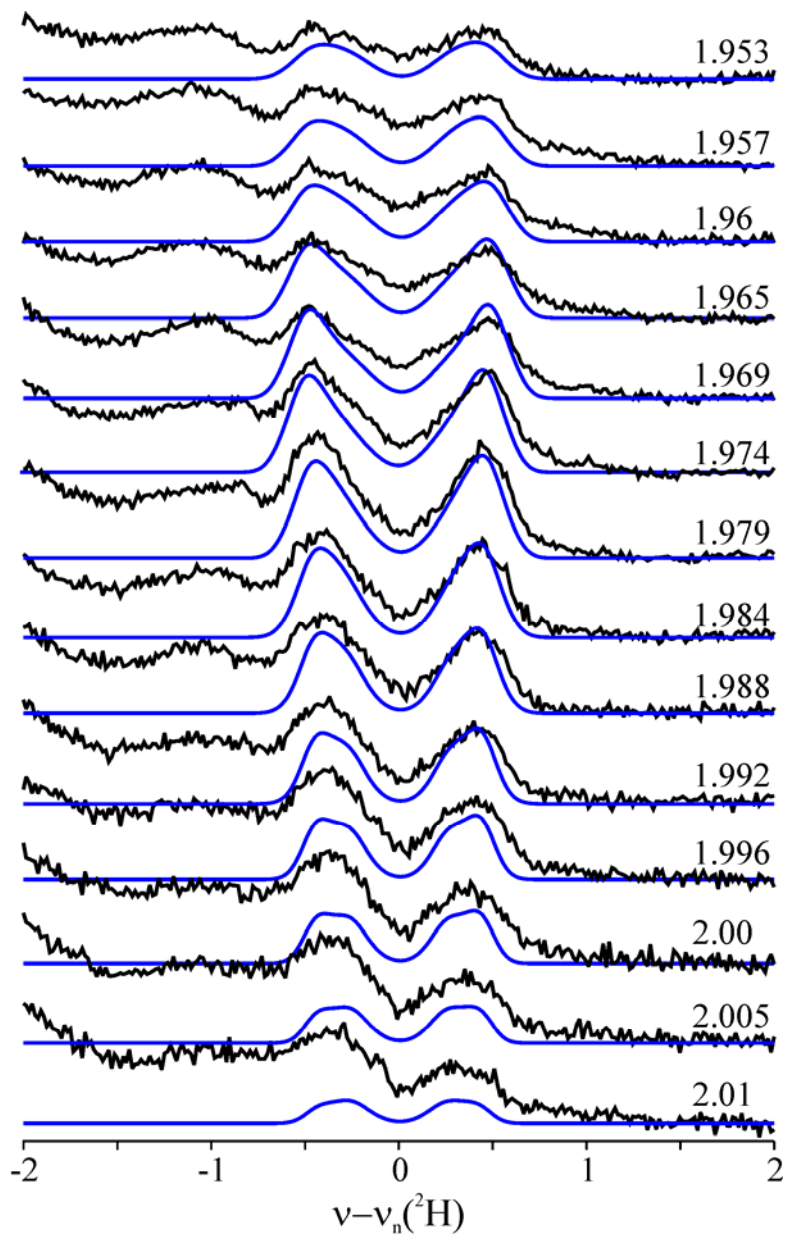
35 GHz echo-detected EPR of [HIPTN<sub>3</sub>N]Mo(CO) (**MoCO**, black trace, inset) and [HIPTN<sub>3</sub>N]Mo(CO) after treatment with [2,4,6-Me<sub>3</sub>C<sub>5</sub>H<sub>3</sub>N]BAr'<sub>4</sub> (Ar' = 2,3-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), in the absence of reductant (<sup>2</sup>H**MoCO**<sup>+</sup>), green trace; residual **MoCO**, black trace). Experimental conditions: microwave frequency, 34.984-34.986 GHz;  $\pi = 200$  ns; repetition rate, 20-80 ms;  $\tau = 600$  ns; temperature, 2 K.

Figure S2



35 GHz Mims  $^{2}\text{H}$  ENDOR spectra measured near the maximum EPR intensity of  $^{2}\text{HMoCO}^{+}$  ( $g = 1.969$ ). The value of  $\tau$ , the time between the first and second pulses in the Mims sequence, is varied from 500 to 1000 ns, which is equivalent to varying the  $^{2}\text{H}$  hyperfine suppression from 2 to 1 MHz (see text). *Experimental conditions.* Microwave frequency, 35.000 GHz; repetition time, 40 ms;  $\pi/2 = 50$  ms;  $t_{\text{rf}} = 30$   $\mu\text{s}$ ; temperature, 2 K; and the RF was randomly hopped. *Simulation parameters.*  $g = [2.010, 1.974, 1.953]$ ;  $g_1 = z$ ; EPR linewidth, 300 MHz;  $\mathbf{A} = [-0.70, -1.15, 1.2]$  MHz; orientation relative to  $\mathbf{g}$ ,  $(\alpha, \beta, \gamma) = (25, 65, 0)$ ;  $\mathbf{P} = [-0.075, 0.034, 0.041]$  MHz; orientation relative to  $\mathbf{g}$ ,  $(\alpha, \beta, \gamma) = (0, 55, 0)$ ; ENDOR linewidth, 0.15 MHz.

Figure S3



35 GHz Mims  $^2\text{H}$  ENDOR field-frequency pattern for  $^2\text{HMoCO}^+$ . *Experimental conditions.* Microwave frequency, 34.968 GHz; repetition time, 40 ms;  $\pi/2 = 50$  ms;  $t_{\text{rf}} = 30$   $\mu\text{s}$ ;  $\tau = 600$  ns; temperature, 2 K; and the RF was randomly hopped. *Simulation parameters.*  $\mathbf{g} = [2.01, 1.974, 1.953]$ ;  $\mathbf{g}_1 = z$ ; EPR linewidth, 300 MHz;  $\tau = 600$  ns;  $\mathbf{A} = [-0.70, -1.15, 1.2]$  MHz; orientation relative to  $\mathbf{g}$ ,  $(\alpha, \beta, \gamma) = (25, 65, 0)$ ;  $\mathbf{P} = [-0.075, 0.034, 0.041]$  MHz; orientation relative to  $\mathbf{g}$ ,  $(\alpha, \beta, \gamma) = (0, 55, 0)$ ; ENDOR linewidth, 0.15 MHz.