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Protonation of the Dinitrogen-Reduction Catalyst [HIPTN$_3$N]Mo^{III} Investigated by ENDOR Spectroscopy

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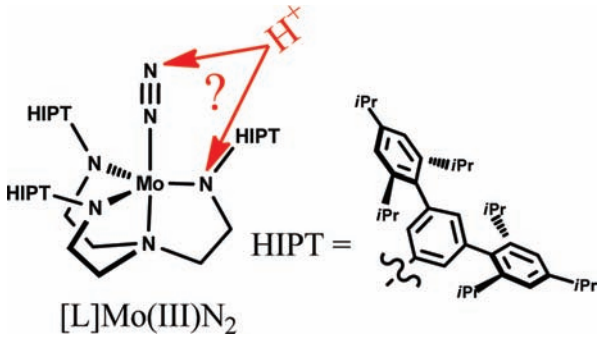
Dinitrogen is reduced to ammonia by the molybdenum complex of L = [HIPTN$_3$N]$^{3-}$ [**Mo**; HIPT = 3,5-(2,4,6-*i*Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$]. The mechanism by which this occurs involves the stepwise addition of proton/electron pairs, but how the first pair converts **Mo**N$_2$ to **Mo**N═NH remains uncertain. The first proton of reduction might bind either at N$_\beta$ of N$_2$ or at one of the three amido nitrogen (N$_{am}$) ligands. Treatment of **Mo**CO with [2,4,6-Me$_3$C$_5$H$_3$N]BAr′$_4$ [Ar′ = 2,3-(CF$_3$)$_2$C$_6$H$_3$] in the absence of reductant generates H**Mo**CO$^+$, whose electron paramagnetic resonance spectrum has greatly reduced *g* anisotropy relative to **Mo**CO. ^{2}H Mims pulsed electron nuclear double-resonance spectroscopy of ^{2}H**Mo**CO$^+$ shows a signal that simulations show to have a hyperfine tensor with an isotropic coupling, $a_{iso}(^2H) = -0.22$ MHz, and a roughly dipolar anisotropic interaction, $T(^2H) = [-0.48, -0.93, 1.42]$ MHz. The simulations show that the deuteron is bound to N$_{am}$, near the **Mo** equatorial plane, not along the normal, and at a distance of 2.6 Å from Mo, which is nearly identical with the (N$_{am}$)^{2}H$^+$—Mo distance predicted by density functional theory computations.

Molybdenum complexes of the L = [HIPTN$_3$N]$^{3-}$ ligand [HIPT = 3,5-(2,4,6-*i*Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$] catalytically reduce dinitrogen to ammonia under mild conditions.[1] The mechanism proposed for this process, a stepwise addition of proton/electron pairs, rests on the intermediate states that have been isolated and characterized to date. However, the mechanism by which the first proton/electron pair converts **Mo**N$_2$ (**Mo** = [L]Mo) into **Mo**N═NH (**Mo**NNH) is unknown. This transformation occurs rapidly in the presence of a reductant, CoCp$_2$ or CrCp*$_2$, and any one of the acids [Et$_3$NH][OTf], [Et$_3$NH][BAr′$_4$], or [2,6-LutH][BAr′$_4$]. Three mechanistic routes have been considered: (i) reduction followed by protonation, either at N$_\beta$ on the dinitrogen ligand or an amido N (N$_{am}$) of [L]; (ii) protonation of either type of nitrogen, followed by reduction; or (iii) proton-coupled electron transfer, again with alternate sites for the proton. To achieve a comprehensive understanding of the reduction mechanism, it is of importance to identify the site at which a proton is most likely to interact (Scheme 1).

Scheme 1



In the absence of a reducing agent, the addition of 1 equiv of LutH$^+$ to **Mo**N$_2$ [ν(NN) = 1990 cm^{-1}] generates a new species, H**Mo**N$_2^+$, with a ν(NN) stretch increased to 2057 cm^{-1}. This shift is consistent with decreased back-bonding to the dinitrogen ligand; however, no new low-energy band is observed, as would be expected if N$_\beta$ of the dinitrogen ligand were protonated. Similarly, when **Mo**CO [ν(CO) = 1885 cm^{-1}] is treated with 1 equiv of LutH$^+$, a new species, H**Mo**CO$^+$, appears with ν(CO) increased to 1932 cm^{-1},[2] again because of diminished back-bonding.[3] Unfortunately, although the amount of protonated **Mo**N$_2$ increases with the amount of LutH$^+$ added, attempts to measure an equilibrium between **Mo**N$_2$ and H**Mo**N$_2^+$ failed because the complexes undergo concomitant decomposition,[3] most plausibly because the loss of protonated [L] is facile.

As an alternative approach to investigating the site at which a proton interacts with **Mo**AB (AB = CO, N$_2$), we have applied electron paramagnetic resonance (EPR) and ^{2}H electron nuclear double-resonance (ENDOR) spectroscopy to samples of these **Mo**AB treated with LutD$^+$ in the absence of a reducing agent.

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(1) Yandulov, D. V.; Schrock, R. R. *Science* (*Washington, DC*) **2003**, *301*, 76–78.

(2) We have been unable to identify any features in the IR spectrum of MoAB, AB = CO, or N$_2$ treated with LutH$^+$ that are consistent with a new NH stretch.

(3) Schrock, R. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 5512–5522.

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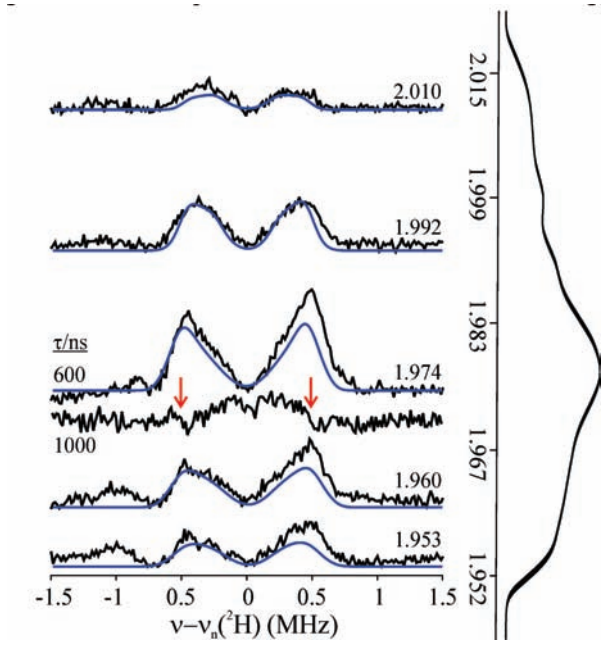

Figure 1. 35 GHz Mims ^{2}H ENDOR field-frequency pattern for ^{2}H**Mo**CO$^+$: A = [−0.70, −1.15, 1.2] MHz; orientation relative to g, (α, β, γ) = (25, 65, 0). Hyperfine suppression holes are indicated with red arrows for the τ = 1 μs spectrum taken at g = 1.974. The EIE spectrum was generated by plotting the intensity of the ν_+ ^{2}H ENDOR response versus field and then applying a spline fit to the data.

Treatment[4] of $S = {}^1/_2$ **Mo**CO with LutH/D$^+$ leads to a new signal in the echo-detected EPR spectrum with a small g spread, **g** = [2.010, 1.974, 1.953] (Figures 1 and S1 in the Supporting Information), in contrast with that of **Mo**CO, whose g values are strongly shifted from the free-electron value, $g_{\|}$ = 3.1 and $g_{\perp}$ = 1.6, and determined by the Jahn−Teller (JT) effect.[5] Only a small percentage of **Mo**CO is converted, consistent with the prior results noted above.

We applied pulsed ENDOR spectroscopy[6] to the new species formed by treatment of **Mo**CO with LutD$^+$ to directly determine the presence and location of a bound deuteron. Mims ENDOR spectra[7] taken at multiple fields across the new EPR signal display a doublet pattern centered at the ^{2}H Larmor frequency, with a hyperfine splitting of approximately $A(^2\text{H}) \sim 1$ MHz (Figure 1), corresponding to $A(^1\text{H}) =$ 6.5 MHz. The assignment of this signal as a ^{2}H ENDOR response is confirmed by its suppression in a spectrum taken with the spacing between the first and second pulses of the Mims sequence of τ = 1 μs. The Mims ENDOR intensity is modulated by the response factor $R \sim [1 - \cos(2\pi A\tau)]$. For an A = 1 MHz coupled deuteron, the Mims ENDOR response should be suppressed when τ = 1 μs, as observed in the spectrum collected at g = 1.974 (Figures 1 and S2 in the Supporting Information).

To confirm that the ^{2}H ENDOR response is associated with ^{2}H**Mo**CO$^+$ and does not arise from the background EPR signal of **Mo**CO, we collected the ENDOR-induced EPR (EIE) spectrum associated with the ^{2}H signal.[7] A 2D field-frequency pattern of ^{2}H ENDOR spectra was collected at multiple points across the range of fields that yield a ^{2}H ENDOR response. The ^{2}H ENDOR signal does not extend past the narrow range of fields assigned to the ^{2}H**Mo**CO$^+$ EPR signal. A fit of the ν_+ peak intensities from the 2D pattern of ENDOR spectra to a spline curve yielded the EIE spectrum of ^{2}H**Mo**CO$^+$ presented in Figure 1, with g values corresponding to those given above.

The 2D field-frequency ^{2}H ENDOR pattern of Figure 1 was simulated[8] to determine the hyperfine tensor of the bound deuteron and, through this, to obtain insight into its location and chemical environment. The pattern is well simulated by a hyperfine tensor having components $A(^2\text{H})$ = [−0.70(10), −1.15(05), 1.2(1)] MHz, which is oriented relative to g by the Euler angles (α, β, γ) = (25, 65, 0).[9] This interaction corresponds to an isotropic coupling, $a_{\text{iso}}(^2\text{H})$ = −0.22 MHz, and a roughly dipolar anisotropic interaction, $T(^2\text{H})$ = [−0.48, −0.93, 1.42] MHz.[10] To test the assignment of the species being studied as Mo−N$_{\text{am}}$(^{2}H$^+$), we performed a density functional theory (DFT) optimization on an N$_{\text{am}}$-protonated **Mo**CO (Figure 2 and Table 1).[11] The low g anisotropy of the new spectrum indicates a strong reduction from the 3-fold symmetry of the parent **Mo**CO. The DFT geometry optimization of the N$_{\text{am}}$-protonated H**Mo**CO$^+$ is consistent with such a symmetry reduction; the length of the Mo−N$_{\text{am}}$-(H$^+$) bond is predicted to be approximately 13% longer than the Mo−N$_{\text{am}}$ bond. This reduction from 3-fold symmetry at Mo readily accounts for the suppression of JT effects implied by the small g anisotropy. If, instead, the oxygen of the axial CO

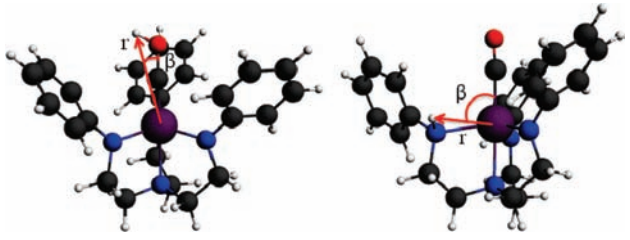

Figure 2. DFT-optimized structures for CO-protonated (left) and N$_{\text{am}}$-protonated (right) **Mo**CO. The predicted values of r and β are 3.65 Å and 13°, respectively, for the CO proton and 2.7 Å and 88°, respectively, for the N$_{\text{am}}$ proton (g_1 is expected to be nearly coincident with the Mo−C bond axis).

(4) A 5 mM solution of **Mo**CO in toluene was treated with 1 equiv of [2,4,6-Me$_3$C$_5$H$_3$N]BAr′$_4$ at room temperature and stirred. Solutions of protonated **Mo**N$_2$ were generated likewise.

(5) McNaughton, R. L.; Roemelt, M.; Chin, J. M.; Schrock, R. R.; Neese, F.; Hoffman, B. M. *J. Am. Chem. Soc.* **2010**, *132*, 8645–8656.

(6) Davoust, C. E.; Doan, P. E.; Hoffman, B. M. *J. Magn. Reson.* **1996**, *119*, 38–44.

(7) Schweiger, A.; Jeschke, G. *Principles of Pulse Electron Paramagnetic Resonance*; Oxford University Press: Oxford, U.K., 2001.

(8) Doan, P. E. The Past, Present, and Future of Orientation-Selected ENDOR Analysis: Solving the Challenges of Dipolar-Coupled Nuclei. In *Paramagnetic Resonance of Metallobiomolecules*; Telser, J., Ed.; American Chemical Society: Washington, DC, 2003; pp 55−81.

(9) The quadrupole splitting for the deuteron is not resolved in the ENDOR spectra, but its incorporation into the simulations is necessary to obtain quality fits. From the simulations, we predict principal values of P = [−0.075, 0.034, 0.039] MHz, with an orientation relative to that of g of (α, β, γ) = (0, 55, 0).

(10) The isotropic and dipolar hyperfine couplings are calculated from the expression $A = a_{\text{iso}} + T$. Absolute signs for the principal hyperfine values were not directly determined. Rather, the sign of a_{iso} must be negative because the maximum dipolar component is positive, $T_3 > 0$.

(11) DFT calculations were performed with the Amsterdam Density Functional (ADF) software package (ADF version 2007.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com) with a BLYP functional in the spin-unrestricted formalism. Geometry optimizations used a TZ2P basis set with a small core potential for all atoms. A reduced structure for **Mo**, in which the HIPT groups were replaced with phenyls, was used for geometry optimization.

Table 1. Selected DFT-Optimized Bond Lengths[a] and Angles for **Mo**CO Protonated Either at an Amido Nitrogen or the Carbonyl Oxygen

	MoH^+		MoN_{am}		MoN_{ax}	MoC	$CMoH^+$		$N_{am}MoN_{am}$		$N_{ax}MoC$
$N_{am}-H^+$	2.690	2.302	2.006	1.977	2.315	2.017	88.2	118.2	110.9	120.8	177.3
$CO-H^+$	3.647	2.057	2.055	2.053	2.348	1.189	13.1	117.7	115.3	116.5	179.3

[a] See ref 4 for computational details.

were protonated, DFT computations (Figure 2 and Table 1) indicate that the resultant species very nearly retains the trigonal symmetry of the parent. Such a complex would exhibit large g anisotropy, like that of **Mo**CO, contrary to observation.

The observed hyperfine tensor also is consistent with N_{am} protonation. Taking the experimental $T_3 = 1.42$ MHz as an effective through-space dipolar coupling constant, $T_3 = 2T = 2g_e\beta_e g_n\beta_n/r^3$, gives $r = 2.6$ Å, consistent with that predicted for a point−dipole interaction between the Mo spin and $N-{}^2H^+$ at the distance calculated from the DFT geometry optimization (2.7 Å, Table 1), $2T = 1.26$ MHz.[12] In contrast, for protonation at the carbonyl oxygen, the DFT geometry gives $r \sim 3.65$ Å, with $2T \sim 0.50$ MHz, much smaller than that observed. More importantly perhaps, the $Mo-{}^2H^+$ vector for CO protonation would lie roughly along the g_1 direction, $\beta \sim 13°$, whereas the $Mo-{}^2H$ vector for N_{am} protonation lies at $\beta = 88°$, in acceptable agreement with the simulations, $\beta = 65°$. In short, both the **g** tensor and the ^2H hyperfine tensor are in agreement with N_{am} protonation and not with CO protonation. An equivalent argument rules out protonation of the "distal" axial nitrogen of [L].

The properties of the ^2H hyperfine tensor for $N_{am}(^2H^+)$ of the $LutH^+$-treated **Mo**CO complex provide support for our recent assignment of the species trapped in frozen solutions when **Mo**N_2 is treated with H_2 gas. This species was assigned as the hydridomolybdenum(III) anion formed by heterolytic cleavage of H_2 and loss of H^+. If, instead, this species were the neutral complex formed by heterolytic H_2 cleavage, with the proton bound as $N_{am}(H^+)$ and the hydride bound to Mo^{III}, it would necessarily show an ENDOR signal equivalent to that seen here from $N_{am}(^2H^+)$, but it does not.

We were unsuccessful in trapping the analogous protonated **Mo**N_2 at low temperature in an EPR tube, with the complex instead presumably decomposing to unidentified species through loss of the protonated organic ligand. Following our earlier discussion of the modes of decomposition of the product(s) of the reaction of H_2 with **Mo**,[13] it seems likely that protonation of **Mo**N_2, like protonation of **Mo**CO, occurs at the amido nitrogen and that the bond between Mo and $N_{am}(H^+)$ of amido-protonated **Mo**N_2 cleaves to form an "arm-off" species that is unstable to total ligand loss, possibly through bimolecular processes. An alternative is that dinitrogen is lost from the cationic species more readily than CO is lost, again with an overall decomposition. The same type of frequency change to the N−N and C−O stretches upon treatment of the respective parent species with $LutH^+$ suggests that protonation occurs at the same site in both systems.

In summary, a combination of EPR/ENDOR spectroscopy and DFT computations shows that treatment of **Mo**CO with the acid $LutH^+$ results in protonation of the amido nitrogen of the $HIPTN_3N^{3-}$ ligand. IR spectroscopic measurements show that **Mo**CO and **Mo**N_2 behave similarly when treated with $LutH^+$ in the absence of reductant, which strongly suggests that N_{am} is protonated in the same way, although protonated **Mo**N_2 is too unstable to be trapped for EPR/ENDOR analysis. That N_{am} is the site of protonation for **Mo**AB, AB = CO and N_2, further indicates that when acid *and* reductant are both present, then reduction of **Mo**N_2 proceeds either by protonation of N_{am}, followed by electron transfer, or by proton-coupled electron transfer. This finding also provides evidence for N_{am} protonation as the first step in the acid-induced decomposition of $[HIPTN_3N]Mo^{III}N_2$.

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Supporting Information Available: Echo-detected EPR spectra, effect of varying τ on the Mims ^2H ENDOR response, and complete 2D field-frequency pattern of Mims ENDOR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

(12) Snetsinger, P. A.; Chasteen, N. D.; van Willigen, H. *J. Am. Chem. Soc.* **1990**, *112*, 8155–8160.
(13) Kinney, R. A.; Hetterscheid, D. G. H.; Hanna, B. S.; Schrock, R. R.; Hoffman, B. M. *Inorg. Chem.* **2010**, *49*, 704–713.