**Supporting Information for**

# Synthesis of DiamidoPyrrolyl Molybdenum Complexes Relevant to Reduction of Dinitrogen to Ammonia

by

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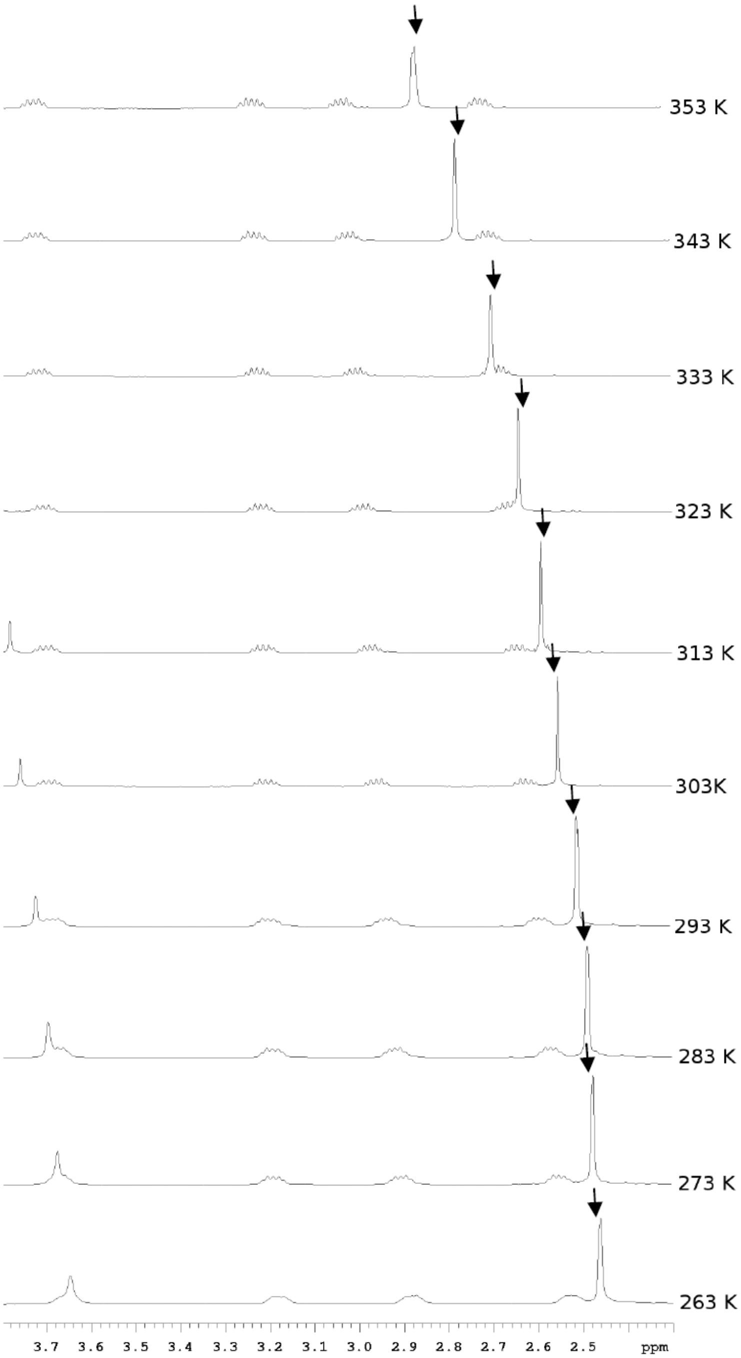

**Figure S1. Temperature-dependent $^1$H NMR spectrum of [$(C_6F_5N)_2$Mespyr]$MoNMe_2$; the arrow indicates the position of the dimethylamide chemical shift**

## Crystallographic Details

Low temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å), for the structures of compounds $[(C_6F_5N)_2Pyr]MoCl$ and $[(C_6F_5N)_2Pyr]MoNMe_2$ and on a Bruker D8 three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Cu Kα radiation ($\lambda$ = 1.54178 Å) for the structure of $[(Ar^{t\text{-}Bu}N)_2Pyr]MoN$, performing $\varphi$- and $\omega$-scans. All structures were solved by direct methods using SHELXS[i] and refined against $F^2$ on all data by full-matrix least squares with SHELXL-97,[ii] following established refinement strategies.[iii] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups).

Compounds $[(C_6F_5N)_2Pyr]MoCl$ and $[(C_6F_5N)_2Pyr]MoNMe_2$ both crystallize in the monoclinic space group $P2_1/c$ with one target molecule per asymmetric unit. Apart from a disorder of one of the two pentafluoro-phenyl rings in the structure of **08186**, structure determination of both compounds was straightforward and without complications. The disorder was refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. In addition, planarity restraints were applied to the disordered aromatic groups. The ratio between the two components of the disorder was refined freely and converged at 0.72(2).

Compound $[(Ar^{t\text{-}Bu}N)_2Pyr]MoN$ crystallizes in the monoclinic space group $P2_1/n$ with one target molecule and 1.5 molecules of fluoro-benzene per asymmetric unit. The half occupied solvent molecule is disordered about the crystallographic inversion center. The four tert-butyl groups show signs of slight disorder. The disorder could not be resolved, however, but similarity restraints as well as rigid bond restraints for displacement parameters were applied to the tert-butyl groups. The solvent molecules were refined with the help of planarity restraints as well as similarity restraints on 1-2 and 1-3 distances to make the two independent molecules geometrically equivalent.

**Table S1**: Crystallographic Information for Structures X, Y, and Z.

| Compound | X | Y | Z |
|---|---|---|---|
| Identification code | $[(C_6F_5N)_2Pyr]MoCl$ | $[(C_6F_5N)_2Pyr]MoNMe_2$ | $[(Ar^{t\text{-}Bu}N)_2Pyr]MoN$ |
| Empirical formula | C30 H23 Cl F10 Mo N4 | C32 H29 F10 Mo N5 | C55 H72.50 F1.50 Mo N5 |
| Formula weight | 760.91 | 769.54 | 928.12 |
| Temperature | 100(2) K | 100(2) K | 100(2) K |
| Wavelength | 0.71073 Å | 0.71073 Å | 1.54178 Å |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | P2(1)/c | P2(1)/c | P2(1)/n |
| Unit cell dimensions | a = 10.0775(5) Å<br>b = 19.4734(9) Å<br>c = 16.1625(8) Å<br>α = 90°<br>β = 107.3480(10)°<br>γ = 90° | a = 8.6519(6) Å<br>b = 16.6172(11) Å<br>c = 21.5630(15) Å<br>α = 90°<br>β = 90.2090(10)°<br>γ = 90° | a = 17.0308(4) Å<br>b = 14.0790(4) Å<br>c = 20.7053(5) Å<br>α = 90°<br>β = 97.678(2)°<br>γ = 90° |
| Volume | 3027.5(3) Å$^3$ | 3100.1(4) Å$^3$ | 4920.1(2) Å$^3$ |
| Z | 4 | 4 | 4 |
| Density (calculated) | 1.669 Mg/m$^3$ | 1.649 Mg/m$^3$ | 1.253 Mg/m$^3$ |
| Absorption coefficient | 0.612 mm$^{-1}$ | 0.516 mm$^{-1}$ | 2.537 mm$^{-1}$ |
| F(000) | 1520 | 1552 | 1972 |
| Crystal size | 0.42 x 0.35 x 0.18 mm$^3$ | 0.48 x 0.35 x 0.04 mm$^3$ | 0.45 x 0.15 x 0.10 mm$^3$ |
| Theta range for data collection | 1.68 to 29.57°. | 1.55 to 29.13°. | 3.61 to 67.73°. |
| Index ranges | -13<=h<=13, -25<=k<=27, -22<=l<=22 | -11<=h<=11, -22<=k<=22, -29<=l<=29 | -20<=h<=20, -16<=k<=16, -24<=l<=24 |
| Reflections collected | 57573 | 78331 | 93103 |
| Independent reflections | 8488 [R(int) = 0.0344] | 8342 [R(int) = 0.0396] | 8719 [R(int) = 0.0269] |
| Completeness to theta = 29.57° | 100.0 % | 100.0 % | 97.9 % |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8978 and 0.7832 | 0.9797 and 0.7898 | 0.7855 and 0.3948 |
| Refinement method | Full-matrix least-squares on F$^2$ | Full-matrix least-squares on F$^2$ | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 8488 / 0 / 418 | 8342 / 498 / 538 | 8719 / 143 / 610 |
| Goodness-of-fit on F$^2$ | 1.069 | 1.062 | 1.026 |
| Final R indices [I>2sigma(I)] | R1 = 0.0249, wR2 = 0.0606 | R1 = 0.0252, wR2 = 0.0592 | R1 = 0.0243, wR2 = 0.0606 |
| R indices (all data) | R1 = 0.0294, wR2 = 0.0640 | R1 = 0.0317, wR2 = 0.0635 | R1 = 0.0252, wR2 = 0.0613 |
| Largest diff. peak and hole | 0.487 and -0.355 e.Å$^{-3}$ | 0.558 and -0.374 e.Å$^{-3}$ | 0.361 and -0.389 e.Å$^{-3}$ |

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i. Sheldrick, G. M. *Acta Cryst.* **1990**, A46, 467.

ii. Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112.

iii. Müller, P. *Crystallography Reviews* **2009**, *15*, 57.