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Dmitry V. Yandulov and Richard R. Schrock*: Studies Relevant to Catalytic Reduction of Dinitrogen to Ammonia by Molybdenum Triamidoamine Complexes

Pages 1103–1117. In view of the difficulty of obtaining high-quality crystals suitable for X-ray diffraction and the difficulty of solving several of the five structures described in the paper, it is desirable to provide a more detailed explanation of the crystallographic procedures. The five structures are [HIPTN₃N]-MoN=NH (**MoN=NH**), {[HIPTN₃N]Mo=NNH₂}[Bar'₄] (**MoN=NH₂⁺**; Ar' = 3,5-(CF₃)₂C₆H₃), {[HIPTN₃N]Mo=NH}[Bar'₄] (**Mo=NH⁺**), [HIPTN₃N]MoNH₃ (**MoNH₃**), and {[HIPTN₃N]Mo(2,6-Lutidine)}[B(C₆F₅)₄] (**Mo(2,6-Lutidine)⁺**). The five structures were solved twice using the same data sets, the first time by Dima Yandulov, the second time by Dr. Peter Müller at MIT. The short description of the crystallographic procedures in the Experimental Section of the paper applies to the first set of solutions. All descriptions below apply to the second set of solutions, which, in some cases, differ slightly from the description in the text of the paper. All bond lengths and angles in the paper are from the second set of solutions with one exception; in Table 2 of the paper, the last set of entries concerning the average angles between the mean-square planes between the amido nitrogens and the aryl rings attached to each amido nitrogen came from the first set of solutions. There were no significant differences in the two sets of solutions. Anyone who would like the cif files from the first set of solutions should contact the corresponding author.

For all structures, 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 K α radiation ($\lambda = 0.71073$ Å), performing ω -scans. All structures were solved by direct methods using SHELXS¹ and refined against F^2 on all data by full-matrix least squares with SHELXL-97.² All nonhydrogen atoms were refined anisotropically. All hydrogen atoms bonded to carbon atoms were included in the model at geometrically calculated positions and refined using a riding model. Unless noted differently below, coordinates for hydrogen atoms bound to nitrogen were taken from the difference Fourier synthesis and refined freely with the help of distance restraints. Isotropic displacement parameters for all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements for the second set of solutions are listed in Table 1 of the paper.

Most of the isopropyl and trifluoromethyl groups (if present) in the structures were disordered, and whenever such a disorder could be modeled successfully, it 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. The relative occupancies for the disordered components were refined freely, while constraining the total occupancy of both components to unity. The crystals giving rise to the datasets for some of the structures diffracted

only to relatively low resolution, which led to a low data-to-parameter ratio in the refinement of those structures. This is a problem encountered relatively frequently in compounds that contain large and flexible ligands. Similarity restraints and rigid-bond restraints for anisotropic displacement parameters were applied to all atoms in those structures in order to counteract the correlation effects arising from the low number of data. All structures contain disordered and/or partially occupied solvent molecules. This leads to noninteger values for the number of carbon and/or hydrogen atoms in the empirical formulas of four of those structures.

Most of the structure of **MoN=NH** (Figure 2 in the paper) behaved normally. The nitrogen atoms of the diazenide ligand showed relatively large anisotropic displacement parameters, which could be ascribed either to strong thermal motion or to the presence of a small amount of cocrystallized **MoH** in the crystal chosen for the X-ray study. The NNH hydrogen atom could not be located in the difference density map, and therefore, it was not included in the model. (It should be present in Figure 2.)

In **MoN=NH₂⁺** (Figure 3 in the paper) the Mo–N5–N6 fragment is bent only slightly at N5 (Mo–N5–N6 = 175.4(4)°). N $_{\beta}$ of the NNH₂ unit bends away from N1 slightly and toward N2 slightly, concomitant with a small elongation of the respective Mo–N_{amide} bond (Mo–N1 = 1.961(3) Å, compared to Mo–N2 = 1.953(3) Å and Mo–N3 = 1.949(3) Å). The β hydrogen atoms in the diazenido ligand were located in the difference density map and were included in the model and in Figure 3.

In the structure of **Mo=NH⁺** (Figure 4 in the paper), the β hydrogen in the imido ligand was located in the difference density map and was included in the model and in Figure 4.

In the structure of **MoNH₃** (Figure 6 in the paper) the three ammonia hydrogen atoms were located in the difference electron density; however, a free refinement of those positions only with the help of distance restraints was not stable. Therefore, a riding model was employed, constraining the N–H distances and H–N–H angles, but allowing the torsion angle to refine freely.

In the structure of **Mo(2,6-Lutidine)⁺** (Figure 10 in the paper), the 2,6-lutidine lies nearly in the plane formed by N1, Mo, and N4 (the interplanar angle Pyr/N4–Mo–N1 is 8.5°). The angle between the inner aryl ring of the HIPT substituent bound to N1 and the plane of the N1 amide is 91.4°. Although the HIPT substituents adopt orientations that are different from one another, the approximate overall C_s symmetry is apparently sufficient to accommodate both envelope conformations of each of the N(amide)–Mo–N4–C–C rings equally well; the two opposite gauche conformations around the Mo–N4 bond were refined as well-behaved disorder. 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. The relative occupancies for the disordered components were refined freely and converged at a ratio of 60:40.

Data for all five structures, [HIPTN₃N]MoN=NH (02239), {[HIPTN₃N]Mo=NNH₂}[Bar'₄] (02196), {[HIPTN₃N]Mo=NH}[Bar'₄] (02210), [HIPTN₃N]MoNH₃ (03113), and {[HIPTN₃N]Mo(2,6-Lutidine)}[B(C₆F₅)₄] (04086), are also now available to the public at <http://www.reciprocalnet.org/>. The number in parentheses identifies each structure at this site.

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(1) Sheldrick, G. M. *Acta Cryst. Sect. A* **1990**, *46*, 467.

(2) Sheldrick, G. M. SHELXL 97, Universität Göttingen, Göttingen, Germany, 1997.