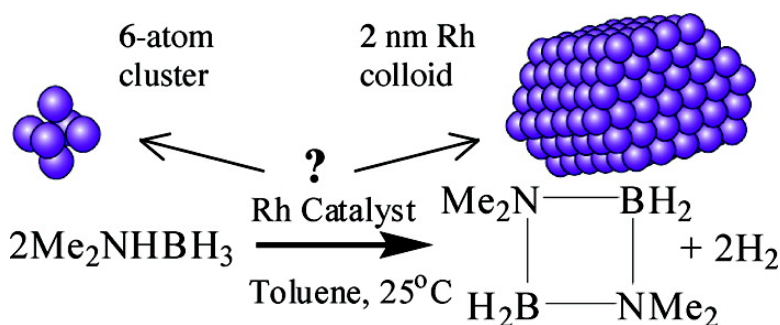


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In Situ XAFS and NMR Study of Rhodium-Catalyzed Dehydrogenation of Dimethylamine Borane

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There has been a recent concerted call from the scientific community for intensive fundamental studies to develop new approaches and novel materials for hydrogen fuel cells, hydrogen production and storage to move our energy economy from one based on fossil fuels to one based upon hydrogen.¹ The challenges put forth have led to our interests in the chemical and physical properties of hydrogen-rich amine borane complexes to develop new materials for onboard storage.² We recently discovered that the kinetics for the thermal dehydrogenation of ammonia borane, NH_3BH_3 , are accelerated when the material is coated into mesoporous silica.³ These results piqued our interest in understanding catalytic processes which accelerate the kinetics of hydrogen release from amine boranes. Recent work from the Manners' group suggested that a heterogeneous rhodium species catalyzed the formation of a cyclic dimer and molecular hydrogen from dimethylamine borane (CH_3)₂-NHBH₃, (DMAB) in solution at room temperature.⁴ They reported that the reaction most likely proceeded by a mechanism involving B–N bond formation catalyzed by Rh(0) colloids. While the evidence at hand seemed to suggest a heterogeneous catalyst, a homogeneous catalytic pathway could not be completely ruled out.

In this communication we present an in situ spectroscopic study utilizing X-ray absorption fine structure spectroscopy (XAFS) and ¹¹B NMR methods to evaluate the rhodium-catalyzed dehydrogenation of DMAB. XAFS provides chemical and structural information of the local environment of the active rhodium species during the reaction, while ¹¹B NMR allows interrogation of the boron-containing species. In XAFS, the strong backscattering from a neighboring heavy atom such as Rh has characteristic amplitude and phase shift functions that are uniquely different from those of adjoining B, N, or C atoms. Thus, XAFS provides a highly sensitive method to detect and measure small atomic clusters of Rh atoms and may help to discriminate between homogeneous and heterogeneous mechanisms. In a complementary experiment, the time-dependent progression of the boron-containing compounds can be monitored by solution-phase ¹¹B NMR to observe the disappearance of DMAB and the formation of the cyclic dimer. Thus, we are able to determine the status of both the catalyst and various B species at different stages of the reaction. We were quite surprised to find that the in situ XAFS results suggest that the active catalyst is a homogeneous six-atom Rh cluster. Furthermore, in situ NMR results suggest that the primary catalytic step involves intramolecular H₂ abstraction, not intermolecular B–N bond coupling.

In situ spectroscopy experiments were performed using toluene solutions containing the catalyst precursor, [Rh(1,5-cod)(μ-Cl)]₂ or Rh(cod) (17 mM), ca. 1.5 mol % Rh, and DMAB (1.1M) prepared under inert atmosphere (see Supporting Information). The samples began to release gas bubbles within seconds of mixing and were immediately transferred into a 4-cm long glass sample holder having Kapton windows for XAFS experiments or into a 5-mm quartz tube for NMR experiments.⁵ The in situ Rh K-edge (23 222 eV) XAFS spectra were collected on the bending magnet beamline (PNC-CAT,

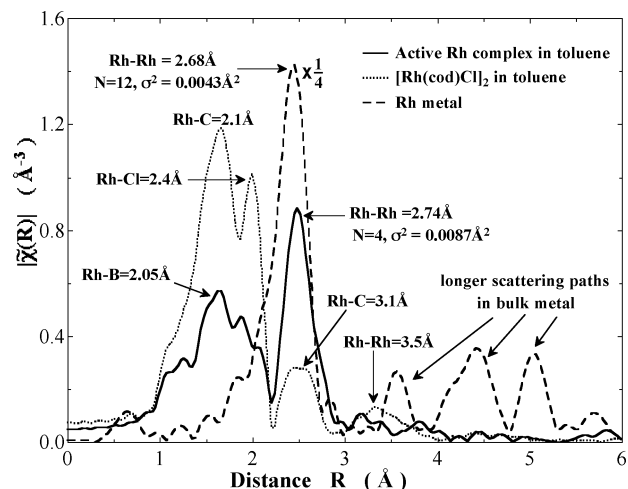


Figure 1. Radial structure plots for the active Rh complex in toluene at $t = 34$ min (solid), the fresh Rh(cod) pre-catalyst in toluene (dotted), and Rh metal (dashed), without phase corrections. The phase-corrected Rh–Rh distances, coordination numbers and Debye–Waller factors from a fit to the theoretical standard (FEFF8) are given. The Rh metal spectrum is multiplied by $1/4$ to fit the graph.

Sector 20) at the Advanced Photon Source, Argonne National Laboratory. Data were analyzed using AUTOBK and IFEFFIT routines.⁶ The kinetics of DMAB disappearance were followed using ¹¹B{¹H} NMR spectroscopy run unlocked on a Varian VXR-300 NMR spectrometer operating at 96 MHz.

Analysis of the XAFS spectrum obtained from the solid Rh(cod) gives bond lengths that are in excellent agreement with the bond lengths from the published X-ray diffraction data.⁷ Furthermore, when the Rh(cod) is dissolved in toluene, there is little change in the XAFS spectra compared to those of the neat material, a strong indication that starting ligands are not significantly displaced by toluene. On the other hand, when DMAB is added to the Rh(cod) toluene solution, new features begin to appear in the XAFS spectra over the course of a few minutes with the concurrent observation of gas bubbles. The extended X-ray absorption fine structure (EXAFS) radial structure plot (RSP) for the new rhodium complex is shown in Figure 1, together with that for Rh(0) metal and Rh(cod) in toluene for comparison. The RSP is related to the probability of finding an atom at some radial distance from the central absorbing atom (Rh). This RSP for the active complex was acquired after 34 min of reaction where all Rh was completely soluble in the toluene. The bond distances and coordination numbers given in Figure 1 are determined by fitting the EXAFS spectra to FEFF8 theoretical standards.⁸ As shown in Figure 1, the fitted Rh–Rh distance for the bulk metal, 2.68 Å, is the same as that determined from crystallographic data. In contrast, the Rh–Rh distance in the active complex is significantly longer at 2.74 Å. There are 12 Rh atoms in the first coordination shell for bulk Rh(0) metal, whereas we

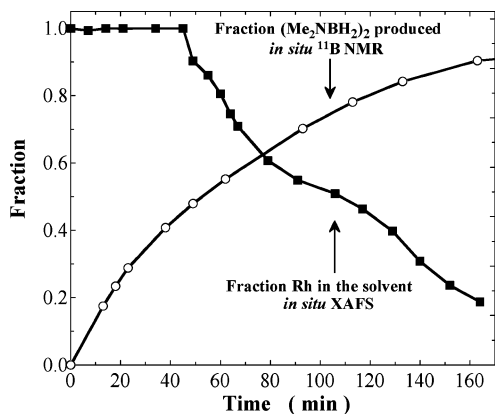


Figure 2. Time-evolving formation of $[\text{Me}_2\text{NBH}_2]_2$ measured by in situ ^{11}B NMR (open circle) and the soluble Rh complex in toluene measured from in situ XAFS edge height (solid square).

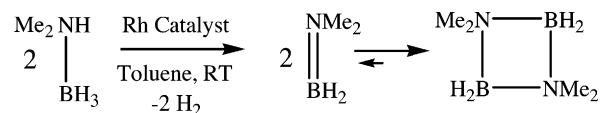
found that the coordination number is 4 for the active complex. Comparison of the RSP plots for the pre-catalyst and the active Rh complex shows that after reaction the chlorides and cyclooctadiene (shown by C peaks) leave the Rh center, and other ligands and a few Rh atoms come into the first shell. In a recent paper the XAFS spectra of a $\text{Rh}(\text{O})_6$ metal cluster and $\text{Rh}_6(\text{CO})_{16}$ on alumina showed that the Rh–Rh distances are 2.68 and 2.75 Å, respectively.⁹ The XAFS spectrum of the $\text{Rh}(\text{O})_6$ metal cluster resembles that of the bulk metal except the amplitude is lower. However, the absorption spectrum of the Rh carbonyl complex shows a significant phase shift due to the longer Rh–Rh distance. The Rh complex observed in our EXAFS spectra also shows a significant phase shift (see Supporting Information). We find that the first-shell coordination number of 4 is consistent with a hexarhodium cluster and the longer Rh–Rh distance is more consistent with ligand-induced relaxation of the Rh–Rh metal bond distance in this small cluster. Hence, we propose that the observed Rh complex has the same Rh_6 cluster core as $\text{Rh}_6(\text{CO})_{16}$ complex,¹⁰ but obviously with different ligands.

To follow the evolution of the Rh species leading to the dehydrogenation of DMAB a series of in situ XAFS spectra were collected at 7-min intervals. In under 14 min, the $\text{Rh}(\text{cod})$ spectra is completely replaced by a spectrum of the new soluble Rh species shown in Figure 1. The time-dependent yield of the total soluble Rh species, determined from the absolute height of the XAFS absorbance edge and the yield of the dimeric product determined by ^{11}B NMR, are compared in Figure 2. Two features are notable, (1) the concentration of the new soluble Rh species remains constant over a period of 45 min during which a large amount of gas is evolved and 45% of the DMAB is reacted; (2) after 45 min the signal from the soluble Rh signal begins to decrease in intensity. We attribute the decrease in the XAFS signal to the precipitation of an insoluble Rh species. What is surprising is that a large portion of the catalytic activity occurs during the time when the soluble Rh species is present.

The precipitation of the active Rh_6 species during the course of reaction may be the result of a ligand exchange process. Ligands that result in lower solubility, e.g., the product, cause the Rh_6 complex to precipitate in the later stages of the reaction. The decrease in solubility of a homogeneous catalyst over the course of the reaction has been reported by Bullock.¹¹ At the beginning of the reaction the catalyst is soluble; however, as the reaction proceeds, the products cause the catalytic species to become less soluble, and it begins to precipitate. At the end of the reaction, the

catalytic material can be recovered, or alternatively more DMAB can be added to bring the catalytic species back into solution.

Results from the ^{11}B NMR experiments permit us to propose a mechanism for the Rh-catalyzed dehydrogenation of DMAB. Specifically, a new ^{11}B resonance at $\delta = 37$ ppm that is not observed in the thermal decomposition reaction grows in initially and then decays over the course of the reaction. We assign the new resonance to a transient dimethylaminoborane $(\text{CH}_3)_2\text{NBH}_2$ species based upon the reported ^{11}B resonance of monomeric $\text{R}_2\text{N}=\text{BH}_2$ species.¹² The resulting monomeric dimethylaminoborane undergoes subsequent thermal dimerization to yield the observed product. This assignment is supported by our observation that the maximum percentage of the $\delta = 37$ ppm species in the reaction mixture is inversely related to the initial DMAB concentration. This observation would be expected for a species that is consumed by second-order pathways.



In sum, combining XAFS and ^{11}B NMR spectroscopies provides a unique set of experimental tools to study the Rh-catalyzed dehydrogenation reaction of DMAB. Our results show that addition of $\text{Rh}(\text{cod})$ to a toluene solution containing DMAB generates a soluble six-atom Rh species. These results suggest a homogeneous catalytic pathway. However, minor rhodium species (<1% of the observed Rh species) may also be present, and further efforts to determine kinetics and additional in situ spectroscopy of this system are underway to help clarify the identity of the catalyst species.

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Supporting Information Available: XAFS and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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