

**Dimethylammonium Hexanoate-Stabilized Rhodium(0) Nanoclusters Identified as True Heterogeneous Catalyst with the Highest Observed Activity in the Dehydrogenation of Dimethylamine Borane**

Supporting Information

*Mehmet Zahmakıran and Saim Özkar*

Department of Chemistry, Middle East Technical University, 06531, Ankara, Turkey

(References cited here are independent of the main text)

#### Experimental:

**Kinetic Studies for the Rhodium(0) Nanoclusters Catalyzed Dehydrogenation of Dimethylamine Borane.** Two sets of experiments were performed at  $25 \pm 0.1$  °C. In the first set, the concentration of DMAB was kept constant at 100 mM (1mmol, 60.7 mg  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  in a total 10 mL solution) and the rhodium concentration was varied in the range of 1.0, 2.0, 3.0 and 4.0 mM by using respective amount of 5 mM rhodium(II) hexanoate solution. In the second set of experiments the rhodium concentration was kept constant at 2.0 mM Rh while the concentration of dimethylamine borane was varied in the range of 50, 60, 75, 90, 100, 125 and 150 mM by dissolving 30.4, 36.4, 45.6, 54.7, 60.7 75.9 and 91.1 mg  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  in a total 10 mL toluene solution, respectively.

**Determination of the Activation Parameters ( $E_a$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ) for the Dehydrogenation of Dimethylamine Borane Catalyzed by Rhodium(0) Nanoclusters.** The catalytic dehydrogenation of 1 mmol DMAB (60.7 mg  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  in a total 10 mL solution) starting with 0.015 mmol  $[(\text{CH}_3(\text{CH}_2)_4\text{CO}_2)_2\text{Rh}]_2$  (10.3 mg, 0.03 mmol Rh) was performed at various temperatures in the range of 20, 25, 30, 35, 40 °C. The values of the rate constant  $k_{\text{obs}}$  for the dehydrogenation of dimethylamine borane were determined from the slope of the linear portion of the dehydrogenation curve divided by the respective rhodium concentration and used to obtain the activation energy  $E_a$  by using Arrhenius plot as well as the enthalpy of activation  $\Delta H^\ddagger$  and entropy of activation  $\Delta S^\ddagger$  by using Eyring-Polanyi plot.

**Catalytic Lifetime of Rhodium(0) Nanoclusters in the Dehydrogenation of Dimethylamine Borane.** The catalytic lifetime experiment was started with 0.005 mmol  $[(\text{CH}_3(\text{CH}_2)_4\text{CO}_2)_2\text{Rh}]_2$  precatalyst (3.4 mg, 0.010 mmol Rh) 50 mmol  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  (3.04 g= in 20 mL of toluene at  $25 \pm 0.1$  °C When no more hydrogen generation was observed, as a control experiment, additional 2.0 mL of 0.50 M DMAB (60.7 mg, 1.0 mmol  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ ) solution in toluene was added into F-P bottle under  $\text{N}_2$  purging and no detectable hydrogen generation was observed over 8 hours. A final total turnover number of 1040 was obtained after about 26 h.

#### Hg(0) and $\text{CS}_2$ Poisoning Experiments:

**(i) Dimethylamine Borane Dehydrogenation Using Hg-Pretreated Precatalyst.** In the nitrogen filled dry-box, 10.3 mg  $[(\text{CH}_3(\text{CH}_2)_4\text{CO}_2)_2\text{Rh}]_2$  (0.03 mmol Rh) precatalyst was weighed into a disposable glass vial and dissolved in 5 mL toluene which was added with 10 mL gas-tight syringe. Elemental Hg (1.08 g, 5.4 mmol, ca. 180 equiv) was then added to the precatalyst solution and the mixture stirred for 24 h. Then the solution was decanted and filtered to remove Hg. Next, Hg-pretreated Rh precatalyst solution (5.0 mL) was added under  $\text{N}_2$  purging to F-P bottle (which had already been attached to line) contains 1.0 mmol DMAB (60.7 mg,  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ ) in 5.0 mL toluene and the dehydrogenation of DMAB was performed in the presence of Hg-pretreated precatalyst at  $25 \pm 0.1$  °C.

**(ii) Dimethylamine Borane Dehydrogenation Using Hg Treated Active Catalyst.** A typical dehydrogenation of 1.0 mmol DMAB (60.7 mg  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ ) in the presence of 0.015 mmol of the  $[(\text{CH}_3(\text{CH}_2)_4\text{CO}_2)_2\text{Rh}]_2$  precatalyst (10.3 mg, 0.030 mmol Rh) was started at  $25 \pm 0.1$  °C When ~ 40 % of conversion of DMAB was reached under  $\text{N}_2$  purging elemental Hg (1.08 g, 5.4 mmol, ca. 180 equiv) was added and the hydrogen pressure was monitored further for 6 hours.

**(iii) Dimethylamine Borane Dehydrogenation Using  $\text{CS}_2$  Treated Active Catalyst.** The same protocol as described in previous section was carried out, but 0.1 equiv.  $\text{CS}_2$  was used instead of elemental Hg.

**Determination of the Number Active Surface Rh Atoms by CS<sub>2</sub> Poisoning of Rhodium(0) Nanoclusters in the Dehydrogenation of Dimethylamine Borane.** All the experiments were carried out in a similar manner: When ~ 40 % of conversion of DMAB was reached (~ 40 min.) in the dehydrogenation of 1.0 mmol DMAB in the presence of 0.015 mmol of the [(CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>)<sub>2</sub>Rh]<sub>2</sub> precatalyst at 25 ± 0.1 °C under N<sub>2</sub> purging an aliquot (0.10-0.50 µL) of CS<sub>2</sub> stock solution (had been prepared by dissolving 0.7 mL CS<sub>2</sub> in 9.3 mL toluene) was added and the reaction was continued for 10 minutes. Then small aliquot from the reaction solution was taken and <sup>11</sup>B NMR spectrum was immediately obtained. The integration of the product ([Me<sub>2</sub>NBH<sub>2</sub>]<sub>2</sub> at 5 ppm) and reactant (Me<sub>2</sub>NH•BH<sub>3</sub> at -14 ppm) resonances was used to calculate the percent conversion of the reaction.

**Nanofiltration Experiment in the Rhodium(0) Nanoclusters Catalyzed Dehydrogenation of Dimethylamine Borane.** At the end of the complete dehydrogenation of 1 mmol DMAB (60.7 mg Me<sub>2</sub>NH•BH<sub>3</sub>) catalyzed by 0.015 mmol [(CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>)<sub>2</sub>Rh]<sub>2</sub> (10.3 mg, 0.030 mmol Rh) at 25 ± 0.1 °C, the experiment was stopped and the F-P bottle was sealed, disconnected from the line and H<sub>2</sub> pressure was released. Then F-P bottle was transferred back into the drybox, and the reaction solution was then filtered by using Dualex<sup>TM</sup> Millipore (200 nm) into a new 22 × 175 mm pyrex culture tube containing a new <sup>5</sup>/<sub>16</sub> in × <sup>5</sup>/<sub>8</sub> in. Teflon coated magnetic stir bar. The culture tube was then sealed inside the F-P pressure bottle and brought outside the drybox and placed in a constant temperature circulating water bath. Next, the F-P bottle was attached to the line (which had already been evacuated for at least 30 min to remove any trace of oxygen and water present) *via* its TFE-sealed Swagelock Quick-Connects and under nitrogen purging 1.0 mmol DMAB (60.7 mg) was added into F-P bottle. Then, the hydrogen pressure was monitored for 2 hours.

**Testing the Redispersibility and Catalytic Activity of Bulk Material Isolated at the end of the Rhodium(0) Nanoclusters Catalyzed Dehydrogenation of Dimethylamine Borane.** At the end of the dehydrogenation of 1.0 mmol DMAB (60.7 mg, Me<sub>2</sub>NH•BH<sub>3</sub>) catalyzed by 0.015 mmol [(CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>)<sub>2</sub>Rh]<sub>2</sub> (10.3 mg, 0.030 mmol Rh) at 25 ± 0.1 °C, the F-P bottle was sealed, disconnected from the line and H<sub>2</sub> pressure was released and transferred into the drybox, the reaction solution was transferred into two centrifuge tubes (5 mL) which were subsequently sealed and brought out of drybox and then centrifuged at 5000 rpm for 2 hours. Then centrifuge tubes were transferred into a Schlenk tube in which they were decanted under N<sub>2</sub> atmosphere and dried under vacuum (10<sup>-3</sup> Torr) for 3 hours at room temperature. The dried samples of black material were transferred back into the drybox, and taken into a new pyrex culture tube containing 4 mL toluene and a new <sup>5</sup>/<sub>16</sub> in × <sup>5</sup>/<sub>8</sub> in. Teflon coated magnetic stir, then stirred at 900 rpm for 2 hours. The sample of black materials was found to be inactive in the dehydrogenation of DMAB. Actually, it is not dispersible in toluene or other polar solvents such as THF, CH<sub>2</sub>Cl<sub>2</sub> even upon warming.

**Characterization of Rhodium(0) Nanoclusters Formed In-Situ During the Dehydrogenation of Dimethylamine Borane.**

(a) <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B-NMR Spectra of the Dehydrogenation Products of Dimethylamine Borane. In a glass vial 0.015 mmol [(CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>)<sub>2</sub>Rh]<sub>2</sub> (10.3 mg, 0.030 mmol Rh) was dissolved in [D<sub>8</sub>]-toluene (1.5 mL) (by gentle warming up to 40 °C, then cooling down to room temperature) and 0.12 mmol DMAB (7.3 mg Me<sub>2</sub>NH•BH<sub>3</sub>) was added as a solid. The mixture was stirred for 3 h at room temperature until the completion of reaction. The <sup>13</sup>C and <sup>11</sup>B- NMR spectra, taken from the reaction solution in [D<sub>8</sub>]-toluene, showed that [(CH<sub>3</sub>)<sub>2</sub>NBH<sub>2</sub>]<sub>2</sub> and [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sup>+</sup>[CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>]<sup>-</sup> are the only two compounds present in 1:1 ratio in the solution and identified. [(CH<sub>3</sub>)<sub>2</sub>NBH<sub>2</sub>]<sub>2</sub>, <sup>11</sup>B NMR: δ = 4.7 ppm (t, J<sub>B-H</sub> = 110 Hz), <sup>13</sup>C NMR: δ = 51.6 ppm;

$[\text{Me}_2\text{NH}_2]^+$ ,  $^{13}\text{C}$  NMR:  $\delta = 49.9$  and  $37.4$  ppm;  $[\text{C}_6\text{H}_{11}\text{O}_2]^-$ ,  $^{13}\text{C}$  NMR:  $\delta = 14.3, 23.1, 26.5, 29.5, 32.7$ , and  $189.0$  ppm.

**(b) ICP-OES and Elemental Analyses of the Dehydrogenation Products.** In a separate experiment 20 mmol DMAB (1.215 g  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ ) and 0.20 mmol  $[(\text{CH}_3(\text{CH}_2)_4\text{CO}_2)_2\text{Rh}]_2$  (140 mg) were combined and heated at  $45^\circ\text{C}$  for 12 hours. The volatiles were removed by evaporation in vacuum<sup>1</sup> at  $45^\circ\text{C}$  for 6 hours leaving a black solid residue. Yield: 0.160 g (94 % assuming 2 equiv  $[\text{Me}_2\text{NH}_2]^+[\text{C}_6\text{H}_{11}\text{O}_2]^-$  per Rh atom). ICP-OES and elemental analyses, calculated (%) for 1 Rh(0) + 2 ( $[\text{Me}_2\text{NH}_2][\text{C}_6\text{H}_{11}\text{O}_2]$ ): Rh, 24.2; C, 45.2; H, 9.01; N, 6.59. Found: Rh, 23.5; C, 43.0; H, 8.9; N, 6.2.

A similar experiment was performed starting with 20 mmol DMAB (1.215 g  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ ) and 0.40 mmol  $[(\text{CH}_3(\text{CH}_2)_4\text{CO}_2)_2\text{Rh}]_2$  (280 mg) in a schlenk tube. The mixture was heated at  $45^\circ\text{C}$  for 12 hours. The gaseous outlet was bubbled through 10 mL methanol in another schlenk tube to trap the  $\text{B}_2\text{H}_6$  product. During the reaction, 0.1 mL aliquots were periodically drawn from the methanol solution and dissolved in 0.5 mL  $[\text{D}_8]$ -toluene for taking  $^{11}\text{B}$  NMR spectrum. The observation of a single peak at  $\delta = 17.9$  ppm in the  $^{11}\text{B}$  NMR spectra due to  $\text{B}(\text{OMe})_3$  shows unambiguously that during the reduction of rhodium(II), the protonation of DMAB leads to the evolution of diborane ( $\text{B}_2\text{H}_6$ ), which is trapped in methanol as  $\text{B}(\text{OMe})_3$ .

**(c) FTIR and XRD Analyses.** The dried samples of black insoluble bulk material obtained in the same way as described in the section Testing the Redispersibility of Bulk Material Isolated at the end of the Rhodium(0) Nanoclusters Catalyzed Dehydrogenation of Dimethylamine Borane was diluted with KBr (1/10) and pressed into a wafer of 15 mm diameter by using an applied pressure of 6-8 tons per square inch for less than 60 s. The FTIR spectrum of isolated and vacuum dried samples of rhodium(0) nanoclusters (KBr pellet) gives absorption bands at  $\nu$  ( $\text{cm}^{-1}$ ) = 1360 vs, 1442 vs for  $\text{CO}_2^-$ , 2900-3000 s for  $\text{CH}_3^-$  and  $-\text{CH}_2^-$  in  $[\text{C}_6\text{H}_{11}\text{O}_2]^-$  and 2700-2800 s for N-H and C-H in  $[\text{Me}_2\text{NH}_2]^+$ . The XRD analysis was performed by making a thin film of the dried samples of black insoluble bulk material, which was stacked on to the surface of sample holder.

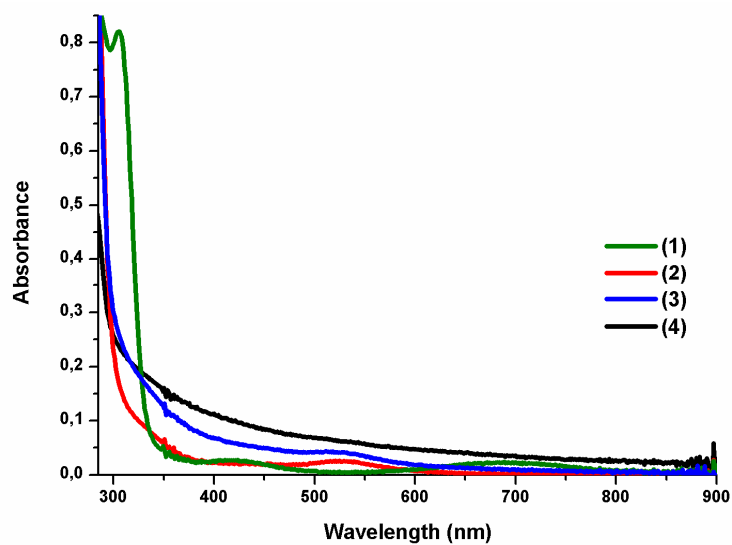
**(d) TEM Analyses.** A typical dehydrogenation of 1mmol DMAB (60.7 mg  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ ) catalyzed by 0.005 mmol  $[(\text{CH}_3(\text{CH}_2)_4\text{CO}_2)_2\text{Rh}]_2$  (3.4 mg, 0.01 mmol Rh) was performed at  $25 \pm 0.1^\circ\text{C}$  in the same way as described in the section General Procedure for Rhodium(0) Nanoclusters Formation and Dimethylamine Borane Dehydrogenation Experiments. TEM samples were harvested from the reaction solution after either 10 % or complete conversion of dimethylamine borane. The reaction solution was dispersed on a chloroform cleaned carbon coated copper grid by dipping it into solution for 5 seconds and evaporating the volatiles under  $\text{N}_2$  flow. Particle size analysis was performed using the public domain NIH Image J 1.62 program<sup>2</sup> developed at the U.S. National Institutes of Health and available on the Internet at <http://rsb.info.nih.gov/nih-image/>. For each particle, the diameter was calculated from the area by assuming that the nanoclusters are circular. Size distributions are quoted as the mean diameter  $\pm$  the standard deviation.

**(e) UV-Visible Electronic Absorption Spectra.** A typical dehydrogenation of 1mmol DMAB (60.7 mg  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ ) catalyzed by 0.005 mmol  $[(\text{CH}_3(\text{CH}_2)_4\text{CO}_2)_2\text{Rh}]_2$  (3.4 mg, 0.010 mmol) was performed at  $25 \pm 0.1^\circ\text{C}$  in the same way as described in the section General Procedure for Rhodium(0) Nanoclusters Formation and Dimethylamine Borane Dehydrogenation Experiments. The small aliquots (100  $\mu\text{L}$ ) were removed by using a gas-tight syringe under  $\text{N}_2$  purging at constant time intervals during the reaction and diluted with toluene before taking the UV-visible electronic absorption spectra.

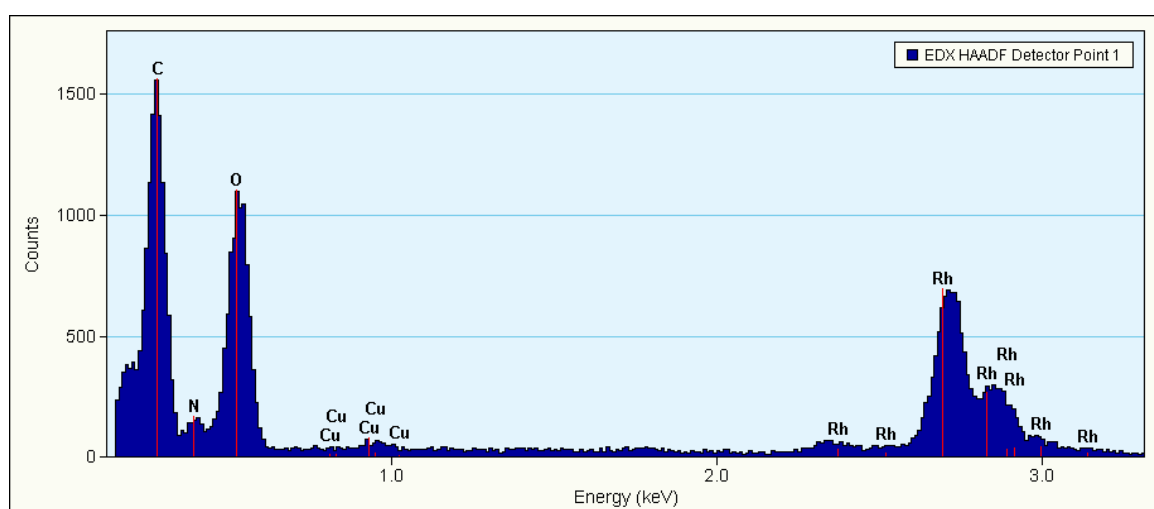
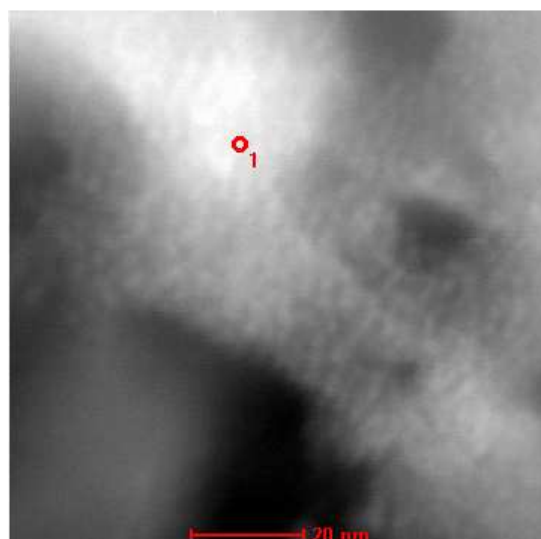
(a)



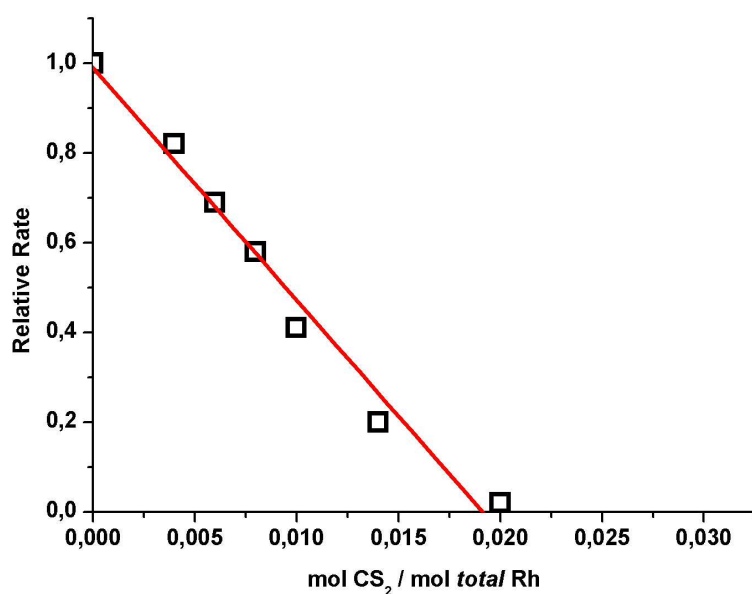
(b)



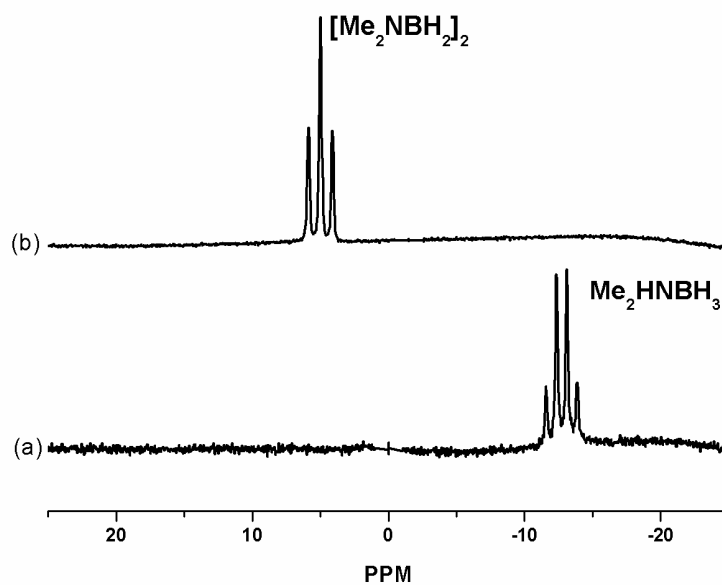
**Figure S1.** (a) The photographs of the reaction mixture in the course of the catalytic dehydrogenation of DMAB borane starting with 1 mmol Me<sub>2</sub>NH•BH<sub>3</sub> and 0.005 mmol [(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>2</sub>Rh]<sub>2</sub> in 10 mL toluene at 25 °C. (b) UV-vis absorption spectra of 0.005 mmol [(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>2</sub>Rh]<sub>2</sub> solution **(1)**, dehydrogenation solution 1 mmol Me<sub>2</sub>NH•BH<sub>3</sub> added into a [(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>2</sub>Rh]<sub>2</sub> solution at t = 0 min. **(2)**, t = 15 min. **(3)**, and t = 35 min. **(4)**.



**Figure S2.** STEM image and STEM-EDX spectrum of hexanoate- and dimethylammonium-stabilized rhodium(0) nanoclusters. STEM-EDS confirms the presence of rhodium on the TEM grid as judged by the  $L_{\alpha 1}$ ,  $L_{\beta 1}$ ,  $L_{b1}$ ,  $L_{b2}$ , and  $L_{g1}$  lines of Rh at 2.69, 2.80, 2.83, 3.0 and 3.14 keV, respectively.

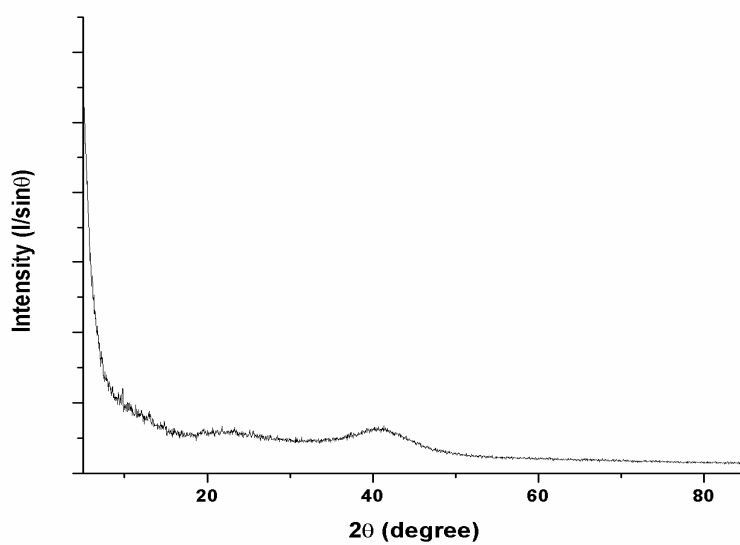


**Figure S3.** The plot of relative rate vs molar ratio of CS<sub>2</sub>/*total* Rh for the dehydrogenation of dimethylamine borane by the rhodium(0) nanoclusters. Rates were determined by the <sup>11</sup>B NMR integration of the product ([Me<sub>2</sub>NBH<sub>2</sub>]<sub>2</sub> at 5 ppm) and reactant peaks (Me<sub>2</sub>NH•BH<sub>3</sub> at -14 ppm). The experimental nonzero rate is passing through a CS<sub>2</sub>/mol of *total* Rh ratio of 0.019 ± 0.001.

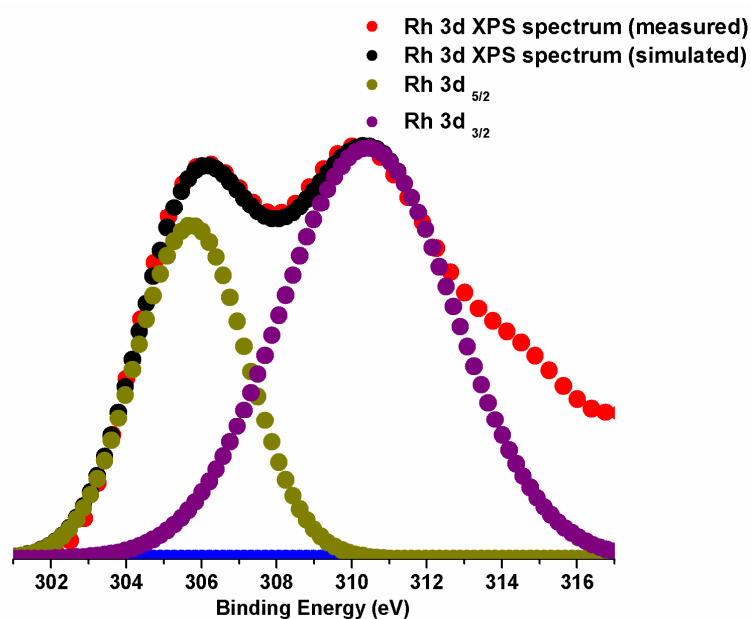


**Figure S4.**  $^{11}\text{B}$  NMR spectra in  $\text{CDCl}_3/\text{toluene}$  of (a) DMAB solution, (b) the reaction solution at the end of dehydrogenation (2.5 h) starting with 0.01 mmol  $[(\text{C}_5\text{H}_{11}\text{CO}_2)_2\text{Rh}]_2$  and 1 mmol  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  in 10 mL toluene at  $25 \pm 0.1^\circ\text{C}$ .

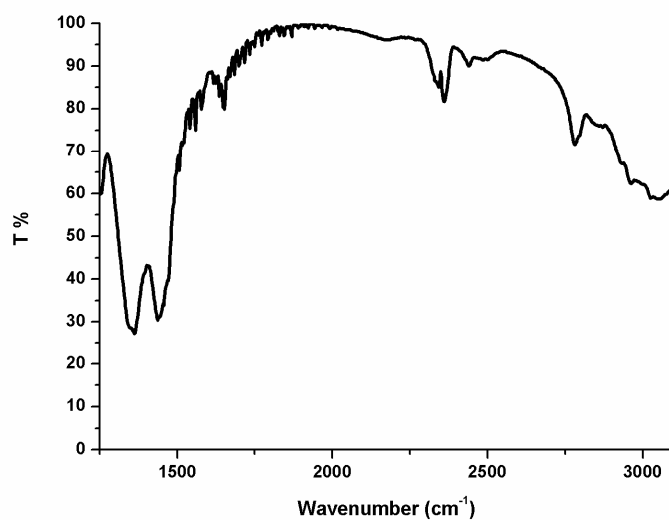




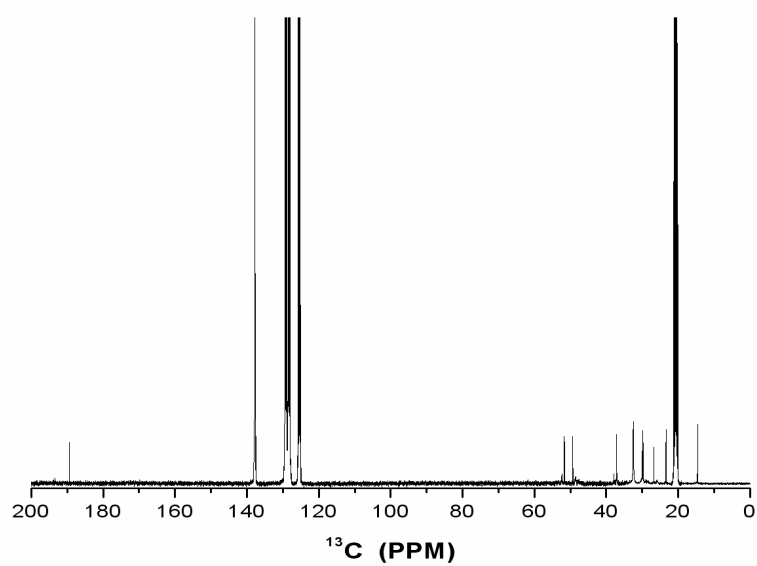
**Figure S5.** Powder XRD pattern of isolated and vacuum dried rhodium(0) nanoclusters at the end of the dehydrogenation of dimethylamine borane starting with 1 mmol DMAB (60.7 mg,  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ ) and 0.005 mmol  $[(\text{CH}_3(\text{CH}_2)_4\text{CO}_2)_2\text{Rh}]_2$  (3.4 mg, 0.010 mmol Rh) at  $25 \pm 0.1$  °C.



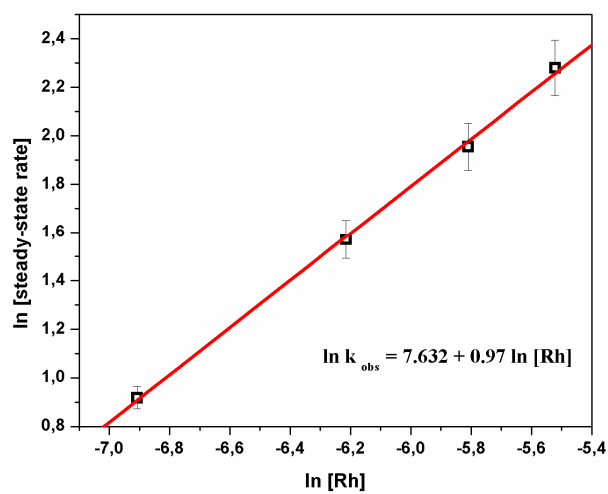
**Figure S6.** Rh 3d X-ray photoelectron spectrum and its simulated peak fitting in the region of 298-316 eV for the isolated and vacuum dried samples of rhodium(0) nanoclusters at the end of the dehydrogenation of dimethylamine borane starting with 1 mmol DMAB (60.7 mg,  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ ) and 0.005 mmol  $[(\text{CH}_3(\text{CH}_2)_4\text{CO}_2)_2\text{Rh}]_2$  (3.4 mg, 0.010 mmol Rh) at  $25 \pm 0.1$  °C.



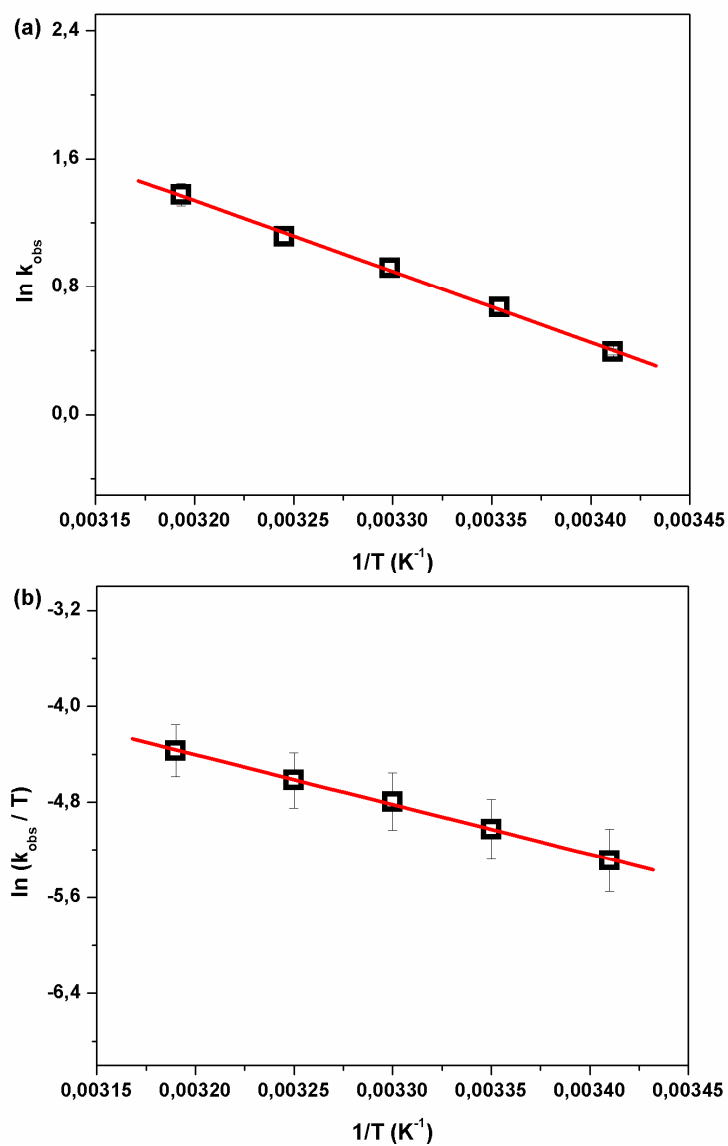
**Figure S7.** Fourier transformed IR spectrum of isolated and vacuum dried sample of rhodium(0) nanoclusters taken from KBr pellet. The absorption bands at 1360 and 1440  $\text{cm}^{-1}$  which are characteristics of carboxylate group and additional bands at 2950 and 3040  $\text{cm}^{-1}$  can be assigned to methyl and methylene groups present in hexanoate anion and weak bands observed in 2750-2840  $\text{cm}^{-1}$  region due to N-H and C-H absorption of the dimethylammonium cation.



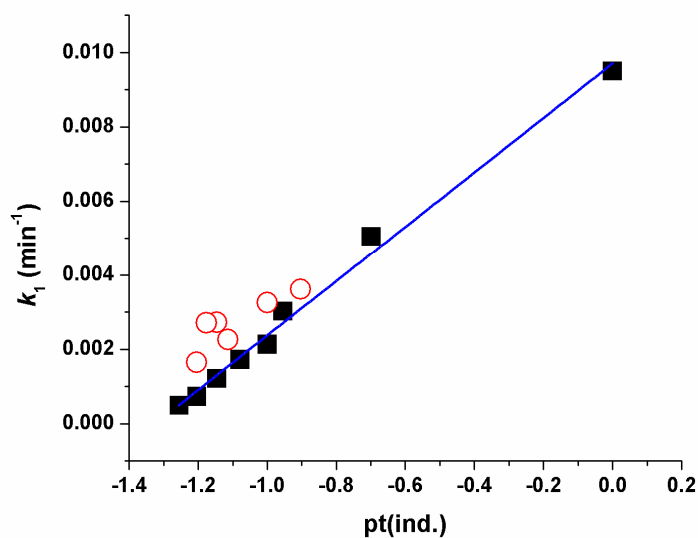
**Figure S8.**  $^{13}\text{C}$ -NMR of the neat reaction mixture from the catalytic dehydrogenation of dimethylamine borane beginning with 0.015 mmol  $[(\text{CH}_3(\text{CH}_2)_4\text{CO}_2)_2\text{Rh}]_2$  and 0.12 mmol  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  in  $\text{C}_6\text{D}_5\text{CD}_3$  (1.5 mL).



**Figure S9.** The plot of dehydrogenation rate versus rhodium concentration for the catalytic dehydrogenation of dimethylamine borane at  $25 \pm 0.1$  °C, both axes are in logarithmic scale. The linear plot gives a slope of  $0.97 \pm 0.03$  which reveals an apparent first-order dependence on the rhodium concentration.



**Figure S10.** (a)  $\ln(k_{\text{obs}})$  vs  $1/T$  graph (Arrhenius plot) in which  $y = 15.52 - 4430 x$ , (b)  $\ln(k_{\text{obs}}/T)$  vs  $1/T$  graph (Eyring plot) in which  $y = 8.92 - 4162 x$  for the dimethylammonium hexanoate-stabilized rhodium(0) nanoclusters catalyzed dehydrogenation of dimethylamine borane



**Figure S11.** The plot of  $k_1$  (min<sup>-1</sup>) versus pt (pt =  $-\log t(\text{ind.})$ ),  $k_1$  values obtained by curve-fitting the identical curves given in whole kinetic studies for the catalytic dehydrogenation/dehydrocoupling of dimethylamine borane.

## References

(1) <sup>1</sup>H NMR analyses of [Me<sub>2</sub>NBH<sub>2</sub>]<sub>2</sub>, obtained by sublimation at 25 °C under N<sub>2</sub> onto a 0°C coldfinger, <sup>1</sup>H NMR (CDCl<sub>3</sub>): 3.1-1.9 ppm (q, br, BH<sub>2</sub>), 2.3 ppm (s, CH<sub>3</sub>) and for Me<sub>2</sub>NHBH<sub>3</sub>, 2.0-1.0 ppm (q, BH<sub>3</sub>), 2.6 ppm (d, CH<sub>3</sub>), 4.3 ppm (br, NH).

(2) Hutchison, J.E.; Woehrle, G.H.; Özkar, S.; Finke, R.G. *Turkish J. Chem.*, **2006**, 30, 1.