Electronic Supplementary Information

Aminopropyltriethoxysilane stabilized ruthenium(0) nanoclusters as isolable and reusable heterogeneous catalyst for the dehydrogenation of dimethylamine-borane

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General and Materials: All operations were carried out using standard Schlenk tube or Fischer–Porter bottle techniques or in a glovebox under argon. Solvents were purified just before use by distillation under a nitrogen atmosphere: THF over sodium benzophenone, pentane over calcium hydride. 1,5-Cyclooctadiene (cod) 3-aminopropyltriethoxysilane (3-APTS), $RuCl_3.3H_2O$ and dimethylamine-borane (DMAB) were purchased from Aldrich. H_2 from Air Liquid; all were used without purification. Ru(cod)(cot) was prepared according to literature procedure.[1]

Characterization: ATR-IR spectra from 3-APTS and isolated solid ruthenium(0) nanoclusters were recorded on a Perkin-Elmer GX 2000 spectrophotometer.The TEM experiments were performed at the "Service Commun de Microscopie Electronique de L'Université Paul Sabatier" on a JEOL 200 CX-T electron microscope operating at 200 kV with a point resolution of 4.5 Å. HRTEM observations were carried out with a JEOL JEM 2010 electron microscope working at 200 kV with a resolution point of 2.5 Å. Specimen for TEM and HRTEM analysis were prepared in a glove box, by slow evaporation of a drop of each crude colloidal solution deposited onto a holey carbon covered copper grid. The particle size analyses were done by using NIH *Image J 1.62* program 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 spherical. Size distributions are quoted as the mean diameter ± the standard deviation. The XPS analysis was performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al Kα radiation (1486.6 eV, with the X-ray

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tube working at 15 kV and 350 W and a pass energy of 23.5 keV). NMR spectra were recorded in THF-d_8 on Bruker Avance DPX 300 MHz spectrometer (300.1 MHz for ^{1}H NMR; 75.6 MHz for ^{13}C NMR; 96.3 MHz for ^{11}B NMR). Tetramethylsilane was used as the internal reference for ^{1}H and ^{13}C NMR chemical shifts. $BF_3{\cdot}(C_2H_5)_2O$ was used as the external reference for ^{11}B NMR chemical shifts.

Synthesis of 3-Aminopropyltriethoxysilane Stabilized Ruthenium(0) Nanoclusters: The solution containing Ru(cod)(cot) (100 mg, 0.318 mmol) and 3-APTS (1.0 equiv./Ru, 74 µL) in 30 mL of freshly distilled and degassed THF in a Fischer–Porter bottle was pressurized with 3 bar H_2 at ambiant temperature during 12 hours under vigorous stirring. During this time the solution changed from yellow to dark brown. The solution was then concentrated by solvent evaporation before pentane addition to favor the colloid precipitation, and the supernatant solution was removed by filtration. The solid was further washed with pentane (3 × 20 mL) and dried under vacuum, giving then rise to the colloid as a black powder. EA (% wt): 38 % Ru, 38 % C, 21 % Si, 5 % H, 4 % N.

Determination of the Catalytic Activity of Ru(0)/APTS in the Dehydrogenation of Dimethylamine-Borane: Before starting to the experiment, the Schlenk (20 mL) containing a 6 mL of 3.73 mM Ru(0)/APTS in THF ($2.24.10^{-5}$ mol of Ru) and Teflon-coated stir bar was placed on a magnetic stirrer and thermostated to 25.0 ± 0.5 °C by circulating water through its jacket from a constant temperature bath (Lauda RL6). Then, a graduated, glass cylinder tube filled with water was connected to the Schlenk tube to measure the volume of hydrogen gas evolved from the reaction. Next, 32.8 mg (0.54 mmol) of Me_2NHBH_3 were dissolved in 4 mL of THF and transferred into the Schlenk tube containing Ru(0)/APTS (2.24 mM) under argon atmosphere at 700 rpm with constant stirring. The catalytic dehydrogenation of DMAB (54 mM) was monitored by measuring the volume of hydrogen gas evolved at constant pressure by determining the decrease in the water level of the glass tube which was connected to the Schlenk tube. When no more hydrogen generation was observed, the experiment was stopped; the Schlenk was taken under partial vacuum and disconnected from the line. Then the Schlenk was transferred back into the glovebox. An approximately 0.5 mL aliquot of the reaction solution in the culture tube was withdrawn with a 9 in. glass Pasteur pipette and added to THF-d_8 in an individual glass ampoule. The solution was then transferred into a quartz NMR sample tube (Norell S-500-QTZ), which was subsequently sealed and then brought out of the glovebox. The ^{11}B NMR spectrum of this solution showed that $Me_2NH_3BH_3$ at -12.5 ppm is completely converted to $[Me_2NBH_2]_2$ at 5 ppm (Figure *ESI*-1).

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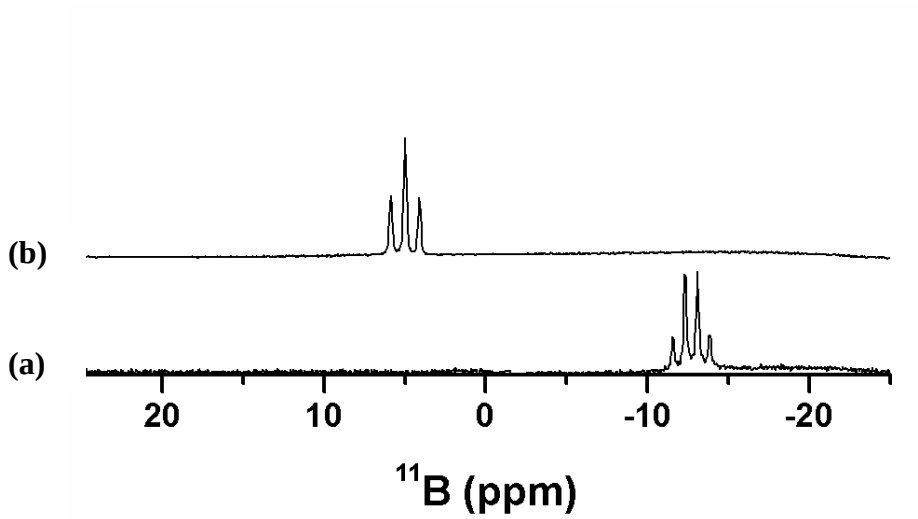

Figure S1. ^{11}B NMR spectra in THF-d_8 of (a) DMAB solution and (b) the aliquot removed at the end of the reaction.

Hg(0) Poisoning Experiment: A typical dehydrogenation of 54 mM DMAB (32.8 mg Me_2NHBH_3) in the presence of 2.24 mM Ru(0)/APTS in 10 mL THF was started at 25 ± 0.1 °C. When ~ 50 % of conversion of DMAB was reached under Ar purging elemental Hg (1.08 g, 5.4 mmol, 240 equiv.) was added. After the addition of elemental Hg, hydrogen evolution was not observed at the end of 6 hours monitoring the reaction.

Isolability and Reusability Experiments: After the first run of dehydrogenation of 54 mM DMAB catalyzed by 2.24 mM Ru(0)/APTS at 25 °C, the catalyst was isolated by evaporating the reaction solution under vacuum (10^{-3} Torr) at room temperature.[2] The dried samples of Ru(0)/APTS were transferred into the glovebox and weighted. Then, they were used again in the dehydrogenation of 54 mM DMAB under the same conditions of first run (Figure ESI-2).

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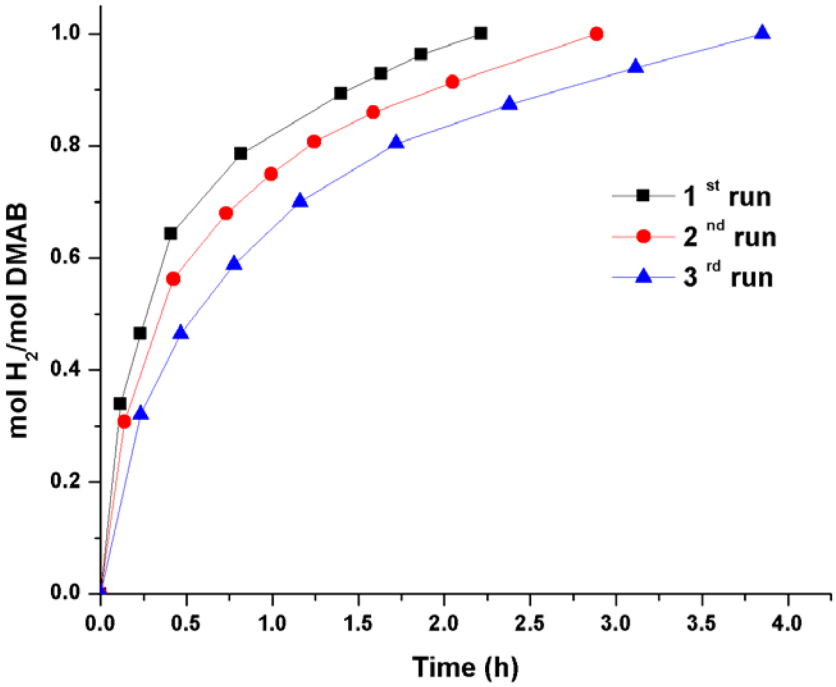

Figure S2. mol H_2/mol DMAB versus time graph for Ru(0)/APTS catalyzed dehydrogenation of DMAB up to third runs.

References

[1] P. Pertici and G. Vitulli, *Inorg. Syn.*, 1983, **22**, 176–81.

[2] ^{11}B NMR spectrum of isolated and vacuum dried dispersion of Ru(0)/APTS shows no signal indicative of the presence of any borane products on nanoclusters surface.

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