Electronic Supplementary Information for:

Highly-Active and Poison-Tolerant Pt_{12} Sub-nanocluster Catalyst for Reductive Amination of Aldehydes with Amines

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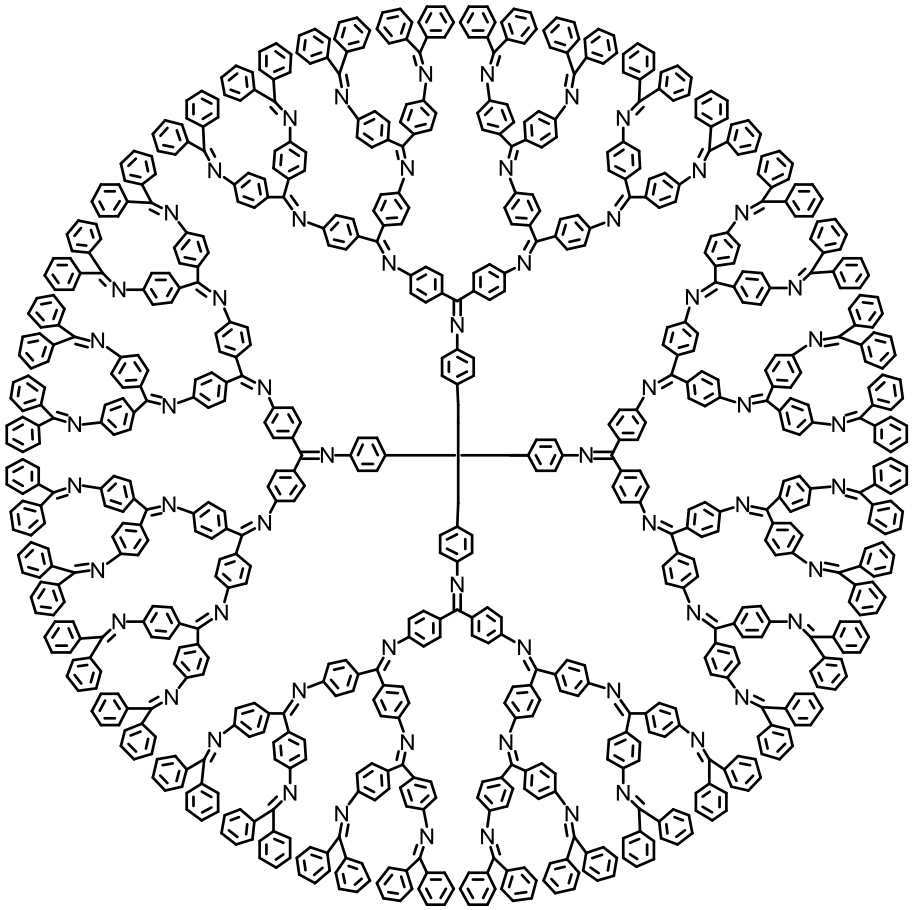
1. Structure of TPM G4 dendrimer



2. Materials and chemicals

A tetraphenylmethane-core phenylazomethine dendrimer with four generations (**TPM G4 dendrimer**) was synthesized by a previously reported method.[1] Methanol of LC/MS grade for, dehydrated acetonitrile of the grade for organic synthesis and pyrrolidine were purchased from Kanto Chemical Co., Inc., and used without further purification. Dehydrated dichloromethane of the grade for organic synthesis and aniline were purchased from Wako Chemical Co., Inc., and used without further purification. *p*-Tolualdehyde and 2-phenylethylamine were purchased from Tokyo Chemical Industry Co., Ltd. Platinum(IV) chloride was purchased from Aldrich. Sodium borohydride was purchased from Kanto Chemical Co. Inc., The 175 nm purified mesoporous carbon (**GMC**) was purchased from Aldrich.

3. General methods

The ^{1}H NMR spectra were measured by a Bruker AvanceIII 400 at 400 MHz. The ^{1}H NMR chemical shifts were referenced to tetramethylsilane (TMS: 0.00 ppm) as the internal standard.

4. Experimental details

Preparation of Pt catalysts

Pt_{12}@TPM G4/GMC: All processes were conducted under a dry nitrogen atmosphere. A 29 µl solution (12 equimolar amount for the TPM G4 dendrimer) of $PtCl_4$ (3 mmol l^{-1}) in acetonitrile was added to a 2.4 ml solution of TPM G4 (3 µmol l^{-1}) in dichloromethane-acetonitrile (1:1). After stirring for 30 min, 10 µl (61 equiv relative to the platinum) of a sodium borohydride solution (0.53 mol l^{-1}) in methanol was added to the solution. Just after the addition, the solution was added to a 1ml stirred suspension of GMC (1.67 mg) in dichloromethane-acetonitrile (1:1) in a sample tube for the following hydrogenation reactions to afford a dispersion of Pt_{12}@TPMG4/GMC.

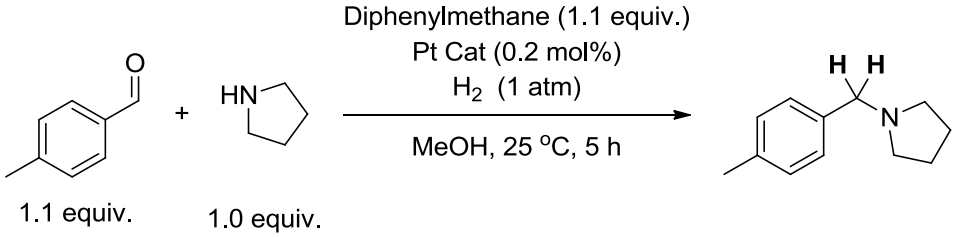
Pt (2.2±0.8 nm)/GMC: All processes were conducted under a dry nitrogen atmosphere. A 29 µl solution of $PtCl_4$ (3 mmol $l^{-1)}$ in acetonitrile was added to a 0.45 ml solution of

dichloromethane-acetonitrile (1:1). After stirring for 30 min, 10 μl (61 equiv relative to the platinum) of a sodium borohydride solution (0.53 mol l^{-1}) in methanol was added to the solution. After stirring for 1 hour, the solution was added to a 1 ml stirred suspension of GMC (1.67 mg) in dichloromethane-acetonitrile (1:1) in a sample tube for the following hydrogenation reactions to afford a dispersion of Pt/GMC.

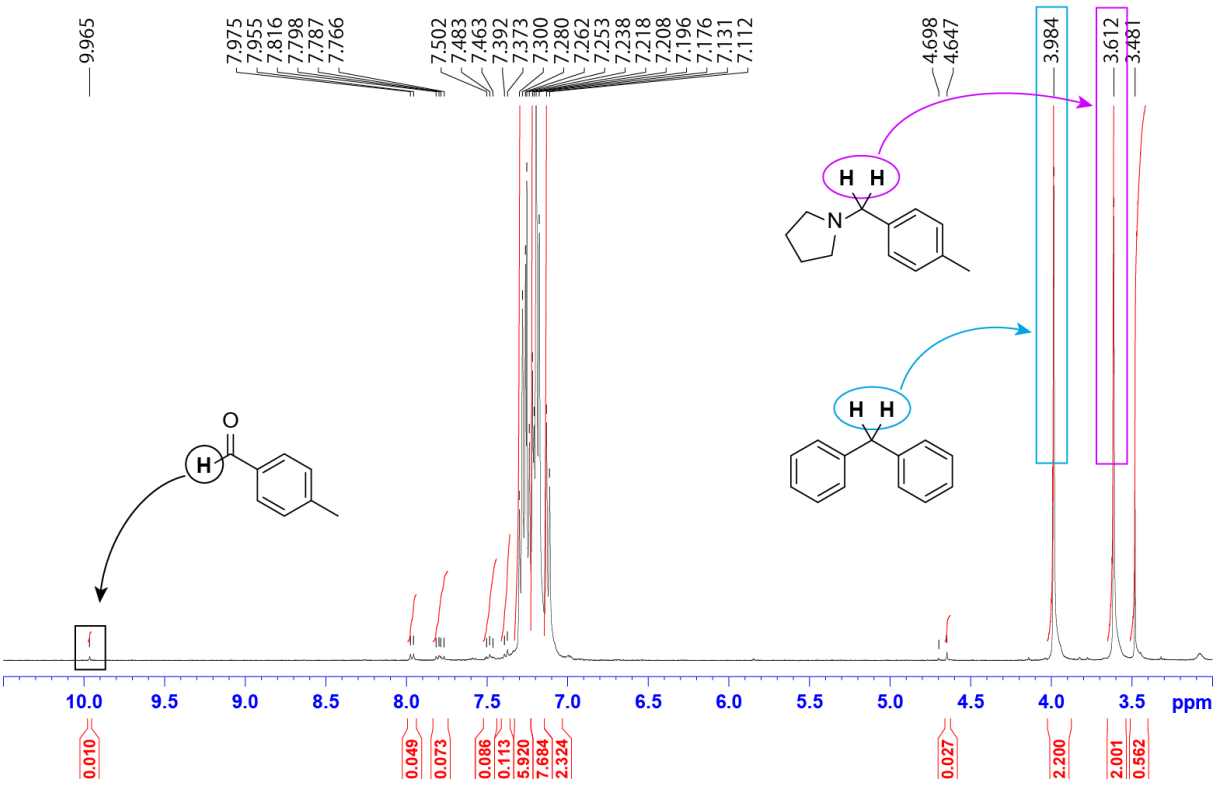
Typical procedure for Pt catalyzed reductive amination: All processes were conducted at room temperature under atmospheric pressure. After removal of the solvent in the sample tube with the catalyst (Pt_{12}@TPMG4/GMC or Pt/GMC) solution under reduced pressure, the flask was charged with dry nitrogen. A 303 μl (3.09 mg, 0.0435 mmol) pyrrolidine solution (30.9 mg, 0.435 mmol) in methanol (3 mL), 306 μl (5.76 mg, 0.0479 mmol) *p*-tolualdehyde solution (57.6 mg, 0.479 mmol) in methanol (3 mL), 308 μl (8.06 mg, 0.0479 mmol) diphenylmethane solution (80.6 mg, 0.479 mmol) in methanol (3 mL) and 1 ml of methanol were added into the flask by a micropipette. Hydrogen gas was supplied from a balloon. The reaction progress was monitored by ^{1}H NMR after 5 hours. The samples for the NMR measurements were prepared by removal of almost all of the solvent from each of the reaction mixtures under reduced pressure.

5. ^{1}H NMR spectra after reaction

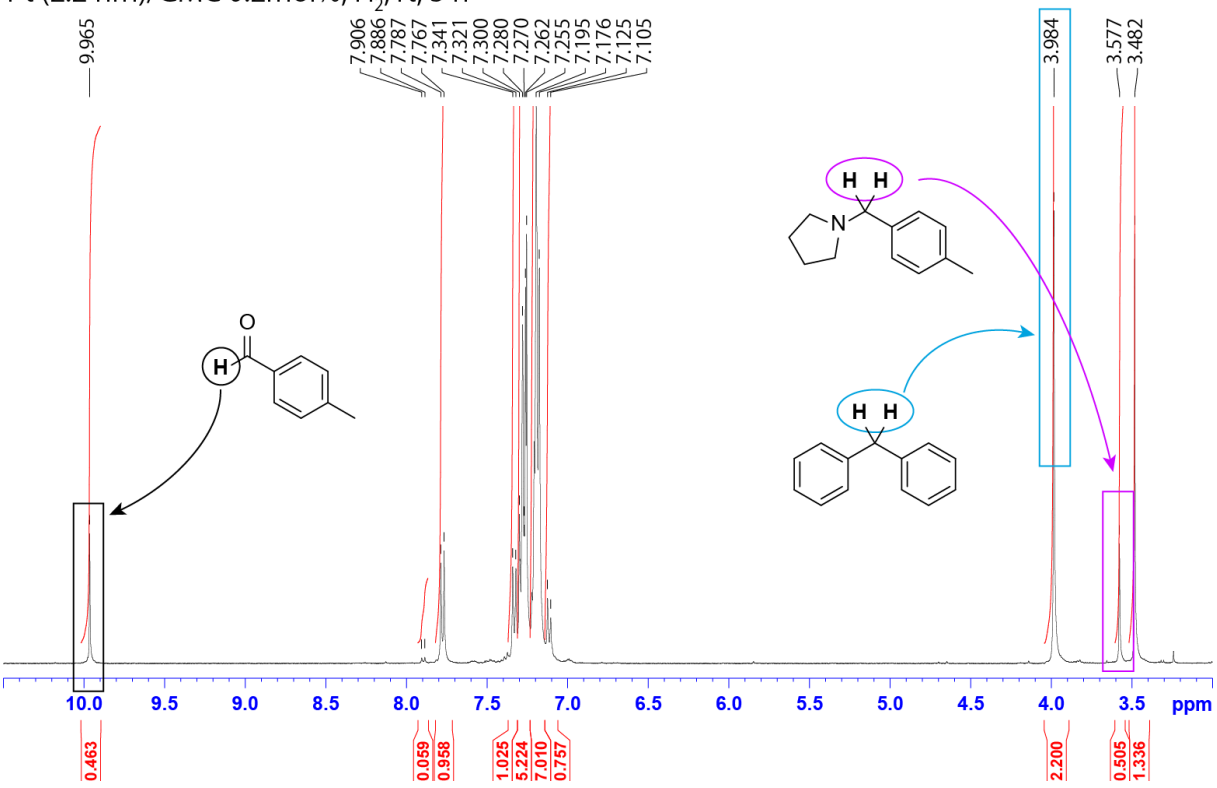
Yields were determined by the ratio of the two methylene peaks of the products and diphenyl methane of internal standard in the ^{1}H NMR spectra. The spectra of reductive amination of aldehyde with pyrrolidine is shown below and all products of the reductive amination are known.[2-4]



Pt_{12}@TPM G4/GMC 0.2mol%, H_2, rt, 5 h



Pt (2.2 nm)/GMC 0.2mol%, H_2, rt, 5 h



6. Reference

1) O. Enoki, H. Katoh, K. Yamamoto, *Org. Lett*., 2006, **8**, 569.

2) W. R. Bowman, P. T. Stephenson, N. K. Terrett and A. R. Younga, *Tetrahedron.*, 1995, **51**, 7959-7980.

3) C. Kay, P. J. Murray, L. Sandow and A. B. Holmes, *Tetrahedron Lett*., 1997, **38**, 6941-6944.

4) B. Sreedhar, S. P. Reddy, K. D. Devi, *J. Org. Chem.* 2009., **74**, 8806-8809.