

Electronic Supplementary Information

Aminoalkoxo-supported heteroleptic hexanuclear gallium(III) wheel as a synthon for group 13 heterometallics: A rare sol-gel precursor for mixed Al-Ga oxide as support for gold catalysts

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Experimental

All synthetic manipulations were performed under argon atmosphere using Schlenk tube and vacuum line techniques. Whereas GaCl₃ (Aldrich) was used as received, the Al(OPrⁱ)₃ (Aldrich) was distilled prior to use. *N*-Methyl diethanolamine (Aldrich) was stored over molecular sieves. Solvents were purified on an MB SPS-800 instrument. The FT-IR spectra were recorded either as Nujol mulls (derivatives **1** and **2**) or KBr pellets (powder obtained after hydrolysis of **2**) on a Bruker Vector 22 spectrometer. ¹H NMR spectra were recorded on a Bruker AC-300 spectrometer. Analytical data were obtained from the Centre de Microanalyses du CNRS. TGA/DTA data were collected on a Setaram 92 system in air with a thermal ramp of 5 °C min⁻¹. Powder X-ray diffraction data were obtained with a Siemens D 5000 diffractometer using CuKα radiation. BET surface areas were determined from N₂ adsorption-desorption isotherms obtained on an ASAP 2010 (Micromeritics) after desorbing the samples at 400°C for 3 h. Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2010 LaB6 microscope operated at 200 kV.

Syntheses

Ga₆Cl₆(mdea)₆ (1·2CHCl₃): To a THF suspension of Na₂mdea [prepared freshly by the reaction of NaH (0.23 g, 9.42 mmol) and mdeaH₂ (0.55 cm³, 4.74 mmol) in 25 cm³ THF under reflux for 1h], a solution of GaCl₃ (0.83 g, 4.71 mmol) in THF (40 cm³) was added and the resulting reaction mixture was stirred first at room temperature for 4h and then refluxed for 1h. After the removal of THF under vacuum, the complex was extracted from chloroform (70 cm³). Crystals suitable for X-ray were obtained at room temperature by layering the concentrated chloroform solution (25 cm³) with diethyl ether (25 cm³). Yield, 0.96 g (78%). Anal.: Calcd for C₃₀H₆₆Cl₆Ga₆N₆O₁₂. 2CHCl₃ (1572.7): C, 24.41; H, 4.32; N, 5.34. Found: C, 24.50; H, 4.33; N, 5.36. ν_{\max} (Nujol)/cm⁻¹ 1346w, 1302w, 1264w, 1245w, 1150w, 1096s, 1050s, 1032m, 992s, 922s, 904s, 877s, 762s, 752s, 651s, 589s, 516m, 482m, 450m, 416s. δ_{H} (300 MHz; CDCl₃) 2.49 (s, 36 H, NMe), 2.80 (t, J = 6.2 Hz, 24 H, NCH₂), 3.81 (m, 24 H, OCH₂).

Ga₂Al₄(O)₂(mdea)₂(OPrⁱ)₁₀ (2·2CHCl₃): To a clear solution of **1** (0.53 g, 0.34 mmol) in chloroform (45 cm³) was added the freshly prepared solid NaAl(OPrⁱ)₄ [from NaH (0.05 g, 2.08 mmol) and Al(OPrⁱ)₃ (0.45 g, 2.20 mmol) in 20 cm³ toluene and 5 cm³ PrⁱOH under reflux for 1h]. A turbid solution was obtained. Addition of six equivalents of Al(OPrⁱ)₃ (0.45 g, 2.20 mmol) resulted in to a clear solution. The resulting reaction mixture was stirred first at room temperature for 6 h and then refluxed for 1 h. After removal of NaCl by filtration, toluene was removed under vacuum from the filtrate. The obtained colourless mass was dissolved in 8 cm³ of chloroform. Colourless plate-like crystals suitable for X-ray were obtained at - 20 °C from this chloroform solution. Yield, 0.72 g (53%). Anal.: Calcd for C₄₀H₉₂Al₄Ga₂N₂O₁₆. 2CHCl₃ (1343.2): C, 37.52; H, 6.99; N, 2.08; Al, 8.03; Ga, 10.38. Found: C, 37.77; H, 7.09; N,

2.20; Al, 8.15; Ga, 10.45. ν_{\max} (Nujol)/ cm^{-1} 1290w, 1261m, 1166s, 1137s, 1099s, 1001s, 958w, 908m, 803s, 760m, 710m, 666s, 635s, 557m. δ_{H} (300 MHz; CDCl_3): 1.04, 1.14 (d, $J = 6.2$ Hz, 48 H, terminal CHMe_2), 1.31 (d, $J = 6.2$ Hz, 12 H, bridging CHMe_2), 2.40 (s, 6 H, NMe), 2.69 (br, 8 H, NCH_2), 3.78 (br, 8 H, OCH_2), 3.95, 4.15 (br/sept, 8 H, terminal CHMe_2).

X-Ray crystallography of **1** and **2**

Suitable crystals of **1** were grown from slow diffusion of the diethyl ether to the chloroform solution at room temperature, whereas colourless plates of **2** were obtained from a concentrated chloroform solution at -20 °C. Crystals of **1** and **2** were mounted on an Oxford-Diffraction Gemini diffractometer equipped with an Atlas CCD detector and using Mo radiation. Intensities were collected at 150 K by means of the CrysAlisPro software.¹ Reflection indexing, unit-cell parameters refinement, Lorentz-polarization correction, peak integration and background determination were carried out with the CrysAlisPro software.¹ An analytical absorption correction was applied using the modeled faces of the crystal.² The structures were solved by direct methods with SIR97³ and the refinement was achieved using the CRYSTALS software.⁴ The crystal structure of **2** showed mixed occupancies of Al and Ga atoms on the metallic crystallographic sites. The occupancies were initially refined while the displacement parameters were fixed. They were then fixed to the values they were converging to and the displacement parameters of the Ga and Al atoms were refined with restraints on their displacement parameters.

Hydrolysis of **2**

Complete hydrolyses of the derivative **2** was performed in aqueous medium without using any organic solvent. The solid **2** (5.0 g, 4.53 mmol) was added to boiling de-ionized water (100 cm³) and refluxed for 2 h. The white powder obtained after centrifugation was washed twice each with 20 cm³ of water and ethanol and finally dried at 70 °C for 12 h. Yield, 1.815 g. ν_{\max} (KBr)/cm⁻¹ 3453br, 2959m, 1625m, 1389w, 1260s, 1082s, 1015s, 908s, 836s, 793s, 667s, 546s. The as-prepared powder was calcined at 400 °C for 4 h. Anal.: Found: Al, 24.0%; Ga, 30.13%.

Colloidal gold deposition

Au/Al₄Ga₂O₉ was prepared by colloidal deposition of gold over Al₄Ga₂O₉ support, using glassware covered with aluminium foil. In this procedure, 0.2 mL of a HAuCl₄ solution (0.25 mol L⁻¹) was added to 100 mL of water. After 5 min stirring, a 1.3 mL solution of polyvinyl alcohol (0.5 wt.%, obtained by diluting PVA MW 10,000 from Aldrich in de-ionized water) was added. Addition of 2.5 mL of a freshly prepared NaBH₄ solution (0.1 mol L⁻¹) after 10 min. turned the yellow solution red. At this point, 1 g of support (white powder) was added. After 2 h, the purple powder was recovered by centrifugation, repeatedly washed with de-ionized water (1 L) and dried in air at 100 °C overnight. Gold loading was found to be 0.5% by weight. Mean diameter for Au NPs, on size distributions obtained by direct observation on TEM bright field images, was 3.6 ± 0.7 nm.

Au/TiO₂-WGC (Sample A # 84) was purchased from the World Gold Council and used after heating in air for 2h at 250 °C. This treatment did not affect its physico-chemical properties. This sample contained gold particles having average diameter of 3.5±1.5 nm. Gold loading was

1.5% by weight. The titania support (Degussa P25) had a mixture of anatase (80%) and rutile (20%) phases.

Catalytic evaluation

Catalytic evaluation was carried out in round-bottom flasks where *trans*-stilbene (substrate, 1 mmol), the gold catalyst (Au: 2 μmol), methylcyclohexane (MCH, solvent, 20 mL / 155 mmol) and an organic initiator (0.05 mmol/7 μL of a 70% TBHP in water Aldrich solution) were stirred together (900 rpm) at 80 °C for over 60 h in air and at atmospheric pressure. Products resulting from the oxidation of stilbene were analyzed by High Performance Liquid Chromatography (Perkin-Elmer HPLC Series 200), using a Spheri-5 RP-18 220 mm x 4.6 mm x 3 μm C18 reverse-phase column, an acetonitrile/water mobile phase mixture at a constant flow rate of 1.0 mL min^{-1} and a Series 200 UV detector set at 250 nm. External calibration was carried out by injecting standard solutions of the following chemicals in acetonitrile: *trans*-stilbene (97% Avocado), benzil (99% Acros), deoxybenzoin (97% Alfa Aesar), benzaldehyde (98% Acros) and methylcyclohexan-1-ol (96% Aldrich). Alkene conversion and oxidation product yield are ratios of the number of moles of alkene converted and the number of moles of product formed both over the initial number of moles of alkene introduced at the beginning of the reaction. Selectivity is defined as the ratio of yield over conversion.

Reference

- 1 CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.48 (release 15-09-2009 CrysAlis171.NET) (compiled Sep 15 2009, 11:49:04).
- 2 Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897.

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4 Betteridge, P.W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Cryst.* 2003, 36, 1487.

Figures with captions

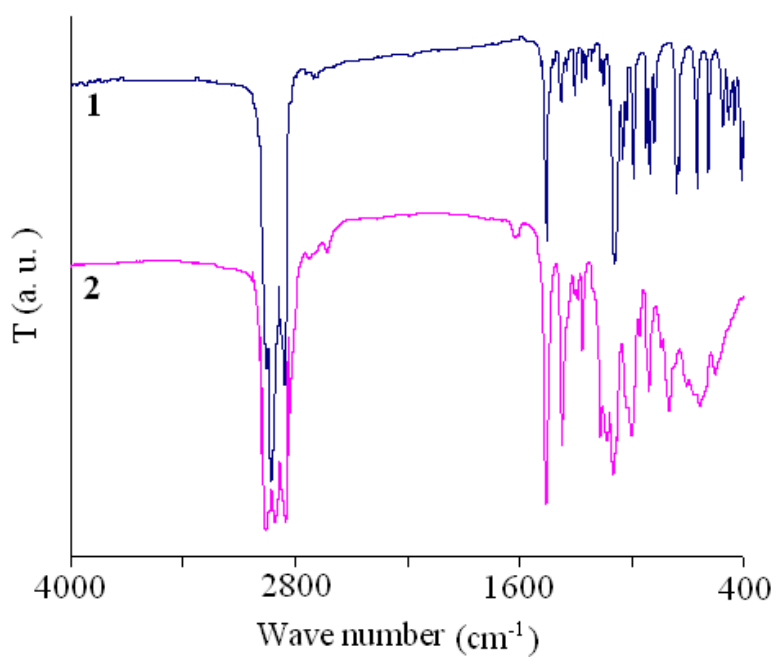


Fig. S1 FT-IR spectra of **1** and **2**.

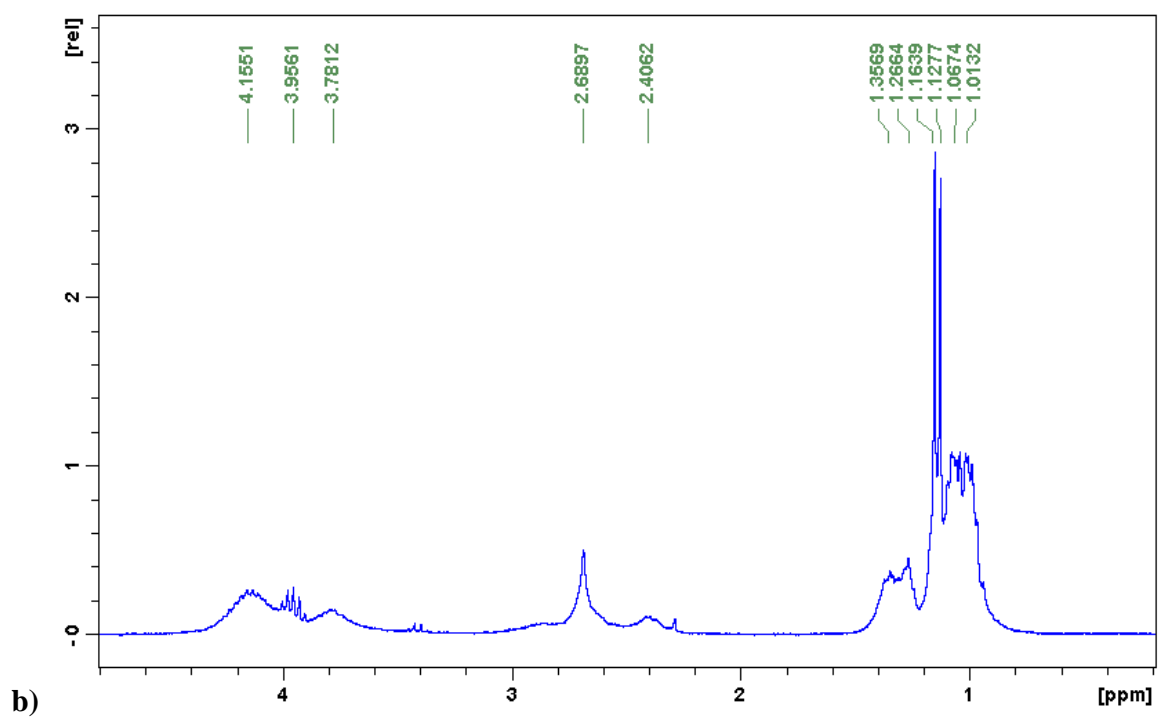
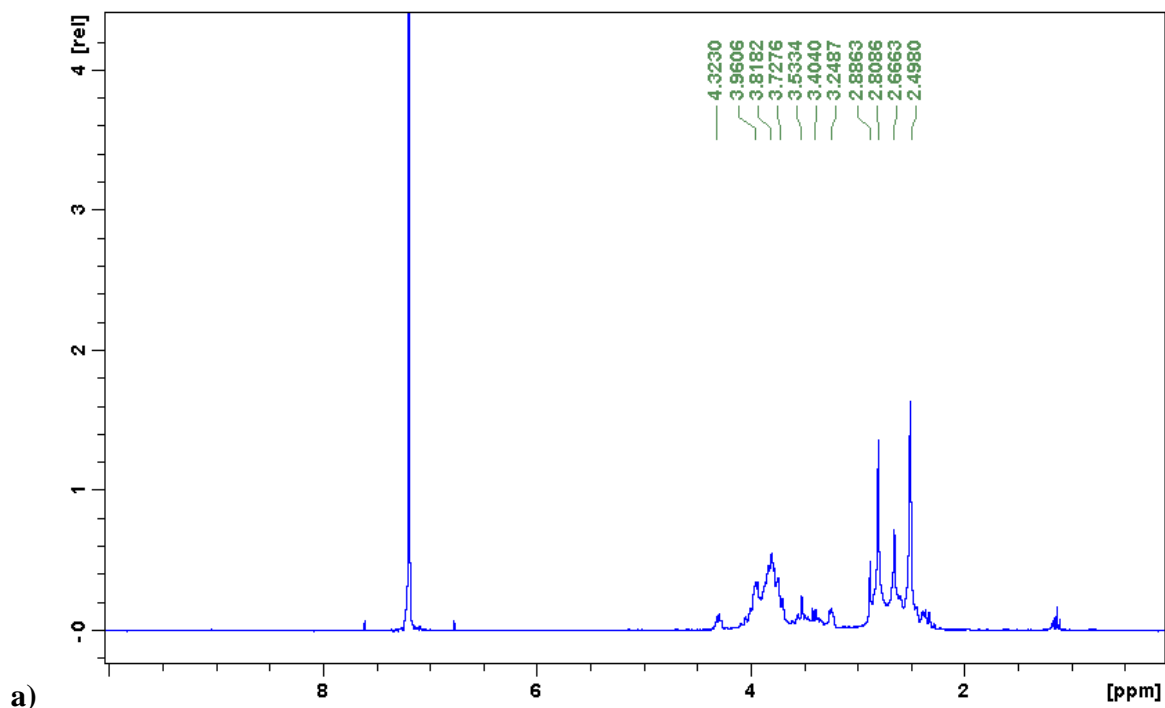


Fig. S2 Room temperature ^1H NMR spectra of **1** (a) and **2** (b).

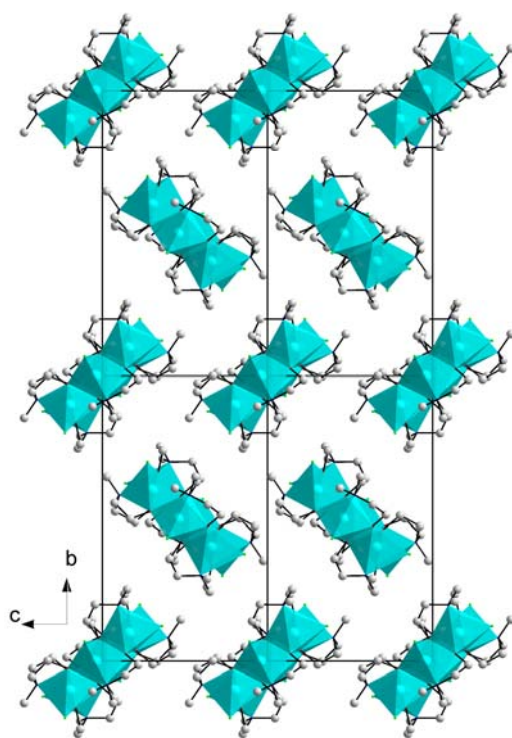


Fig S3. Packing diagram of **1**.

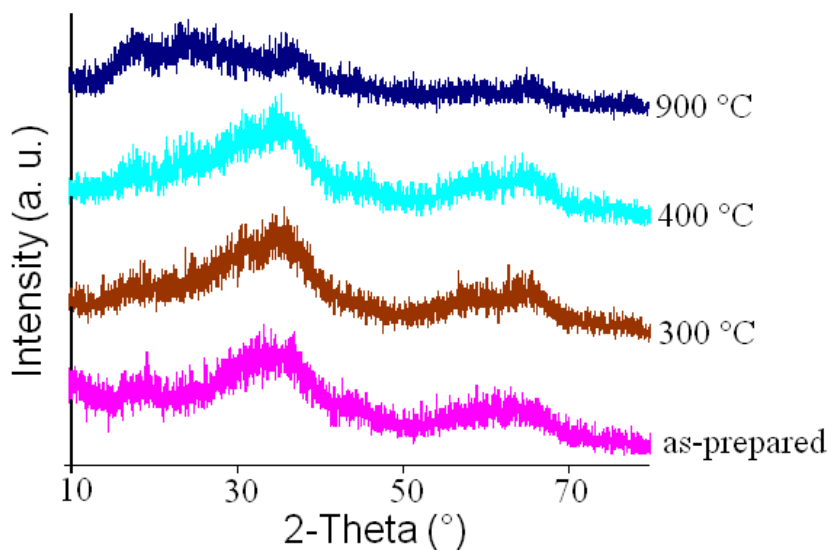


Fig. S4 Variable temperature XRD patterns of powder obtained after hydrolysis of **2**.

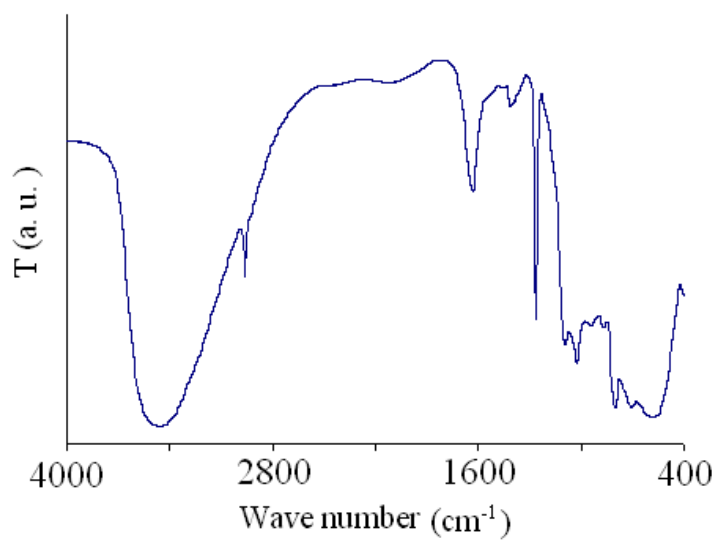


Fig. S5 FT-IR spectrum of the as-prepared powder obtained after hydrolysis of **2**.

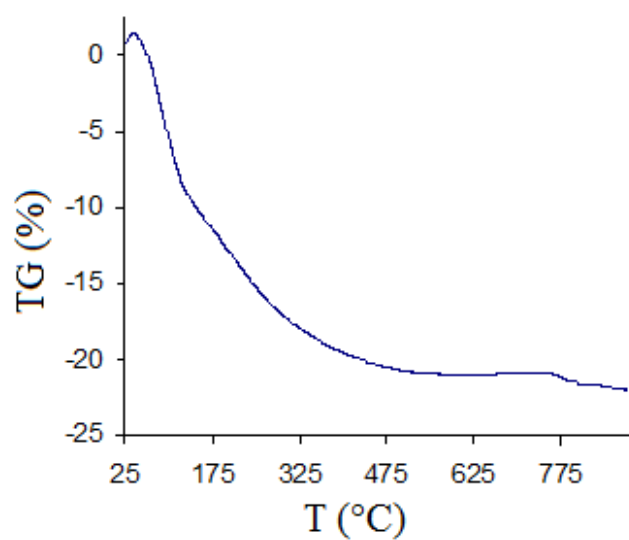


Fig. S6 TG curve of the as-prepared powder obtained after hydrolysis of **2**.

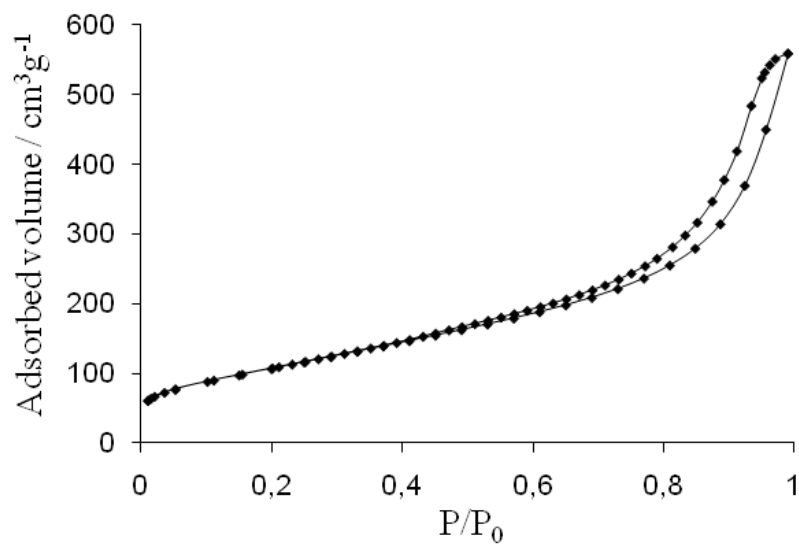


Fig S7. Surface area of Al₄Ga₂O₉ obtained from **2** and calcined at 400 °C for 4 h.