Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Diphosphite ligands derived from carbohydrates as stabilizers for ruthenium nanoparticles: promising catalytic systems in arene hydrogenation

Aitor Gual, M. Rosa Axet, Karine Philippot*,[b]Bruno Chaudret, Audrey Denicourt-Nowicki, Alain Roucoux*, Sergio Castillón and Carmen Claver*[a]

General methods. All syntheses were performed using standard Schlenk or Fischer-Porter techniques under argon atmosphere. $RuCl_3 \cdot H_2O$ (Strem) was purchased and used without prior purification. The other reagents were purchased from Aldrich and most of the solvents from SDS. The solvents were distilled under nitrogen atmosphere. THF and Toluene were refluxed over sodium benzophenone, pentane over calcium hydride, pyridine over potassium hydride, and methanol over magnesium after activation with iodine. All reagents and solvents were degassed under vacuum at liquid nitrogen temperature by 3 vacuum-nitrogen cycles.

[Ru(cod)(cot)] was prepared according to a published procedure.[1] It was purified by recrystallization in pentane and the resulting highly sensitive yellow crystals were stored under argon at -30ºC. The purity was checked by elemental analysis and ^{1}H-NMR spectroscopy.

Elemental analyses of the organic molecules were performed on a Carlo Erba EA-1108 instrument. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer. Chemical shifts are relative to $SiMe_4$ (^{1}H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. All NMR spectral assignments were determined by COSY and HSQC spectra.

Elemental analyses of the nanoparticles were carried out at the "Service Central d'Analyse" (CNRS) in Solaize (69360, France).

Specimens for TEM analysis were prepared by slow evaporation of a drop colloidal solution deposited under argon onto holey carbon-covered copper grids. The TEM experiments were performed using a JEOL 200 CX-T electron miscroscope operating at 200 kV and a Philips CM12 electron microscope operating at 120 kV, with respective

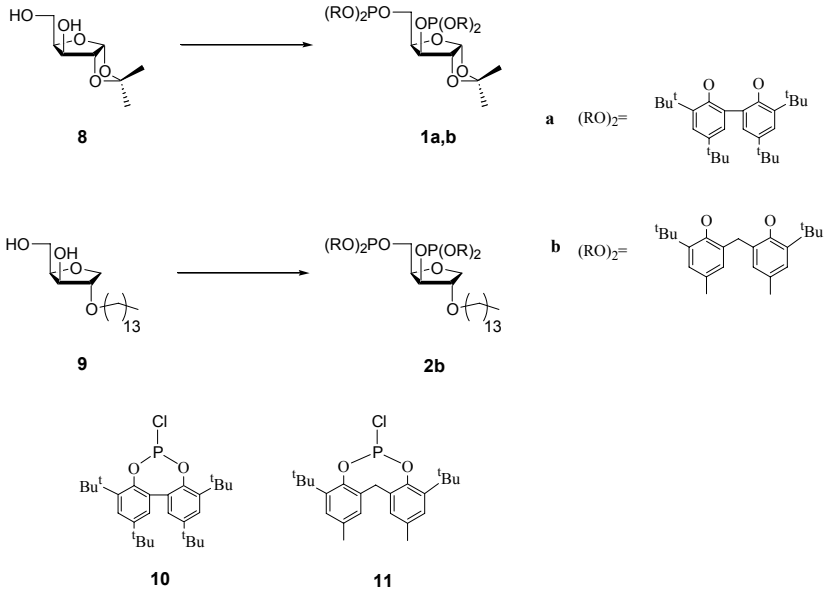
[1] P. Pertici, G. Vitulli , *Inorg. Synth.*, 1983, **22**, 17.

point resolutions of 4.5 and 5Å. Transmission electron microscopy was used as a standard tool of analysis for determining the mean size of ruthenium particles. Size distribution of the particles were determined by manual analysis of enlarged images by measuring at least 200 particles on a given grid to obtain a statistical size distribution as well as a mean diameter.

Gas chromatographic analyses were run with Fisons Instrument (GC 9000 series) equipped with a Chirasil Dex CB column. The detector is at 250ºC and the injector at 150ºC.

Synthesis of diphosphite ligands 1a,b and 2b with a carbohydrate backbone.

Phosphites **1a**,**b** were prepared by reaction of the commercial diol **8** with phophochlohidrites **10**[2] and **11**, respectively, prepared *in situ*, following reported procedures in 75% and 65% yield.[2] Phosphite **2b** was prepared similarly by reaction of diol **9** with phosphochlorhidrite **11** in 50% yield.



General procedure for synthesizing diphosphites from the diols 1, 2. A solution of the xylose derivatives **8** and **9** (1 mmol), previously azeotropically dried with toluene (3x1 mL), in dry and degassed toluene (10 mL) and cooled to 0 ºC, was slowly added to a solution of phosphorochlorohidrites 10, 11 (2.1 mmol), synthesised *in situ* by standard

[2] G.J.H. Buisman, P.C.J. Kamer, P.W.N.M. van Leeuwen, *Tetrahedron: Asymmetry.* 1993, **4**, 1625

procedures, in dry and degassed pyridine (1.5 mL). The mixture was allowed to rise to room temperature and stirred overnight. The mixture was then filtered to eliminate the pyridine salts, and the filtrate was concentrated to dryness. The white foam obtained was purified by flash chromatographic techniques over nitrogen.

Ligand 1a.[2] Purified by flash column chromatography using toluene as eluent to afford **1a** as a white solid, 75 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: ($CDCl_3$, 400 MHz) δ: 1.10 (s, 6H, 2xCH_3), 1.48-1.35 (m, 72H, *o*-C(CH_3)$_3$), 3.95 (m, 1H, H-2), 4.01 (m, 2H, H-5,5´), 4.27 (dt, 1H, J= 5.6, 2.4 Hz, H-4), 4.77 (dd, 1H, J= 7.2, 2.4 Hz, H-3), 5.60 (d, 1H, J= 3.6 Hz, H-1), 7.30-6.70 (m, 8H, aromatic). **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ : 27.0 ($O_2C(CH_3)_2$), 27.2 ($O_2C(CH_3)_2$), 31.6 ($C(CH_3)_3$), 31.8 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$), 35.2 ($C(CH_3)_3$), 36.0 ($C(CH_3)_3$), 62.8 (C-5), 77.0 (C-3), 79.5 (C-4), 84.8 (C-2), 106.0 (C-1), 112.3 ($O_2C(CH_3)_2$), 148.0-124.0 (aromatic). **^{31}P NMR** ($CDCl_3$, 161.97 MHz) δ: 134.8 (s), 143.3 (s). Anal. calcd for $C_{64}H_{92}O_9P_2$: C, 72.02; H, 8.69. Found: C, 71.9; H, 9.3.

Ligand 1b. Purified by flash column chromatography in toluene as eluent to afford **1b** as a white solid, 65 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.50 (2xs, 3H, $O_2C(CH_3)_2$), 1.58 (4xs, 36H, *o*-C(CH_3)$_3$), 1.73 (s, 3H, $O_2C(CH_3)_2$), 2.45 (2xs, 12H, p-CH_3), 3.53 (dd, 2H, J= 12.8, 5.6Hz, $PhCH_2Ph$), 4.53 (m, 2H, $PhCH_2Ph$), 5.04 (m, 3H, H-4, H-5,5´), 5.63 (d, 1H, J=2.4Hz, H-2), 5.79 (d, 1 H, J= 6.0Hz, H-3), 6.31 (d, 1H, J= 3.6 Hz, H-1), 7.41-7.16 (m, 8H, aromatic). **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ : 21.4 (*p*-CH_3), 26.6 (($O_2C(CH_3)_2$), 27.0 ($O_2C(CH_3)_2$), 31.1 (*o*-C(CH_3)$_3$), 34.9 ($PhCH_2Ph$), 61.6 (C-5), 77.3 (C-3), 80.4 (C-4), 84.3 (C-2), 105.3 (C-1), 112.3 ($O_2C(CH_3)_2$), 146.0-125.4 (aromatic). **^{31}P NMR** ($CDCl_3$, 161.97 MHz) δ 129.2 (s), 132.1 (s). Anal. calcd for $C_{54}H_{72}O_9P_2$: C, 69,96; H, 7,83. Found: C, 69.7; H, 8.1.

Ligand 2b. Purified by flash column chromatography (toluene, Rf= 0.60) to afford **2b** as a white solid, 50 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.03 (t, 3H, J= 10.0Hz, O-tetradecyl), 1.33 (m, 22H, O-tetradecyl), 1.55 (s, 36H, *o*-C(CH_3)$_3$), 1.71 (m, 2H, O-tetradecyl), 2.45 (2xs, 12H, p-CH_3), 3.54 (dd, 2H, J= 11.2, 5.6Hz, $PhCH_2Ph$), 3.77 (m, 1H, O-tetradecyl), 3.87 (m, 1H,

O-tetradecyl), 4.12 (d, J= 13.2, H-1´), 4.50 (m, 2H, $PhCH_2Ph$), 4.57 (dd, J= 13.2, 5.6Hz, H-1), 4.77 (m, 1H, H-4), 4.90 (m, 1H, H-5´), 5.00 (d, 1H, J= 5.2Hz, H-2), 5.08 (m, 1H, H-5), 5.75 (dd, 1H, J= 8.4, 4.4Hz, H-3), 7.21-7.17 (m, 8H, aromatic). **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ : 14.3 (O-tetradecyl), 21.3 (p-CH_3), 26.2 (O-tetradecyl), 29.6 (O-tetradecyl), 29.8 (O-tetradecyl), 31.3 (*o*-$C(CH_3)_3$), 32.1 (O-tetradecyl), 34.9 ($PhCH_2Ph$), 62.5 (C-5), 69.9 (O-tetradecyl), 72.3 (C-1), 77.4 (C-3), 80.3 (C-4), 84.3 (C-2), 142.3-125.5 (aromatic). **^{31}P NMR** ($CDCl_3$, 161.97 MHz) δ: 129.3 (s), 131.7 (s). Anal. calcd for $C_{65}H_{96}O_8P_2$: C, 73,14; H, 9,07. Found: C, 72.8; H, 9.19.

Synthesis of the ruthenium nanoparticles. Ruthenium colloids (**Ru/1-Ru/2**) were prepared using the chiral ligands described above as stabilizers (scheme 1).

$$[Ru(cod)(cot)] + 0.1\,\mathbf{L^*} \xrightarrow[3\ bar\ H_2]{solvent,\ r.t.} [Ru/\mathbf{L^*}]_{coll}$$

$$\mathbf{L^*}= 1\text{-}2 \qquad -\ C_8H_{16} \qquad \mathbf{Ru1\text{-}Ru2}$$

In a typical experiment, 150 mg of [Ru(cod)(cot)] (0.476 mmol) were introduced in a Fisher-Porter bottle and left under vacuum for 30 minutes. A solution of 0.1 eq of ligand in 150 mL of THF was cooled to 193K, and then added to Ru(cod)(cot) in the Fisher-Porter bottle. The bottle was pressurized under 3 bar of dihydrogen and the solution allowed to slowly warm to room temperature. Then a vigorous stirring was maintained for 18 hours giving rise to a homogenous dark-brown solution. After elimination of excess dihydrogen, approximately 3 mL of the solution were passed under argon over a small alumina column. The absence of filtrate yellow colour indicated full decomposition of the precursor. The volume of the solution was then reduced to approximately 15 mL. 50 mL of deoxygenated pentane were then added and the resulting mixture cooled to 193 K at which temperature a brown precipitate formed after several hours. Following filtration, the precipitate was washed with deoxygenated pentane (2 x 50 mL) and dried under reduced pressure. The resulting particles were obtained as dark brown powders. In all cases, ruthenium colloids were found to remain stable over time and did not exhibit any sign of decomposition. They were characterized by TEM and Elemental Analysis.

Ru/1a. Elemental analysis (%): Ru = 21.32, C= 44.12, H= 6.11, P = 1.87. Mean diameter (TEM, nm) = 3.98.

Ru/1b. Elemental analysis (%): Ru = 25.71, C= 41.16, H= 5.76, P = 2.34. Mean diameter (TEM, nm) = 2.89.

Ru/2b. Elemental analysis (%): Ru = 29.09, C= 38.24, H= 5.40, P = 1.80. Mean diameter (TEM, nm) = 1.78.

Hydrogenation of meta- and ortho-methylanisole. The Ru-nanoparticles were used as catalyst in the asymmetric hydrogenation of prochiral arenes (See Scheme 2 in the manuscript).

In a typical experiment, methylanisole (154 μL, 1.24 mmol) and 5 mg of nanoparticles (**Ru/1a, Ru/1b or Ru/2b**) were dissolved in 10 mL of the desired solvent in an autoclave. Molecular hydrogen was then introduced until the desired pressure was attained. The reaction was stirred for 16 h. The solution was filtered over celite and the solution analyzed by GC.

TEM characterization of nanoparticles. The sizes of the nanoparticles were determined by TEM (transmission electron microscopy).

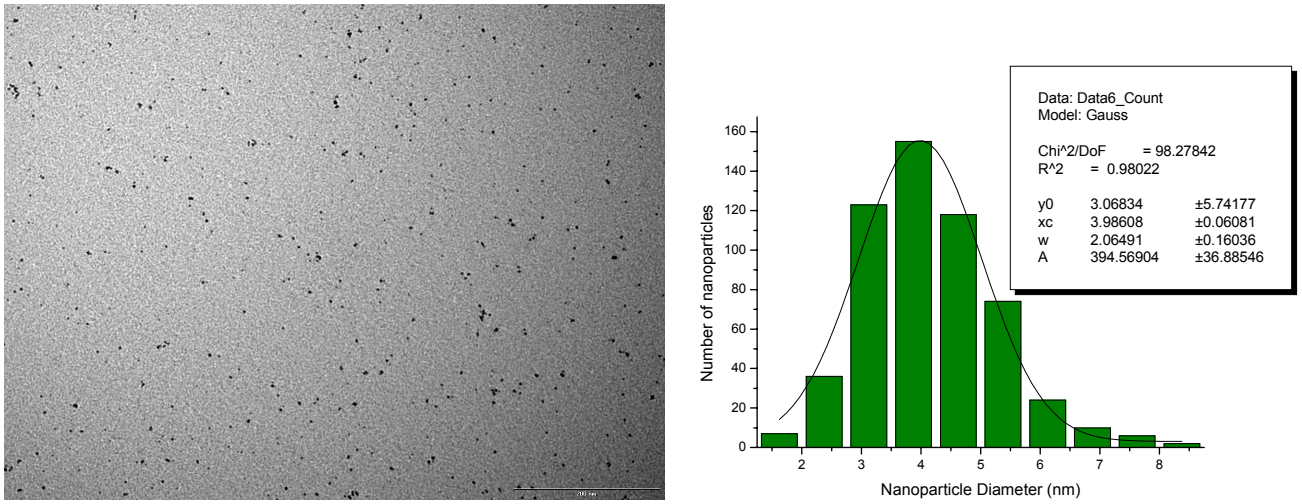


Figure 2. TEM micrograph and size histogram of Ru colloid **Ru/1a** stabilized by ligand **1a**.

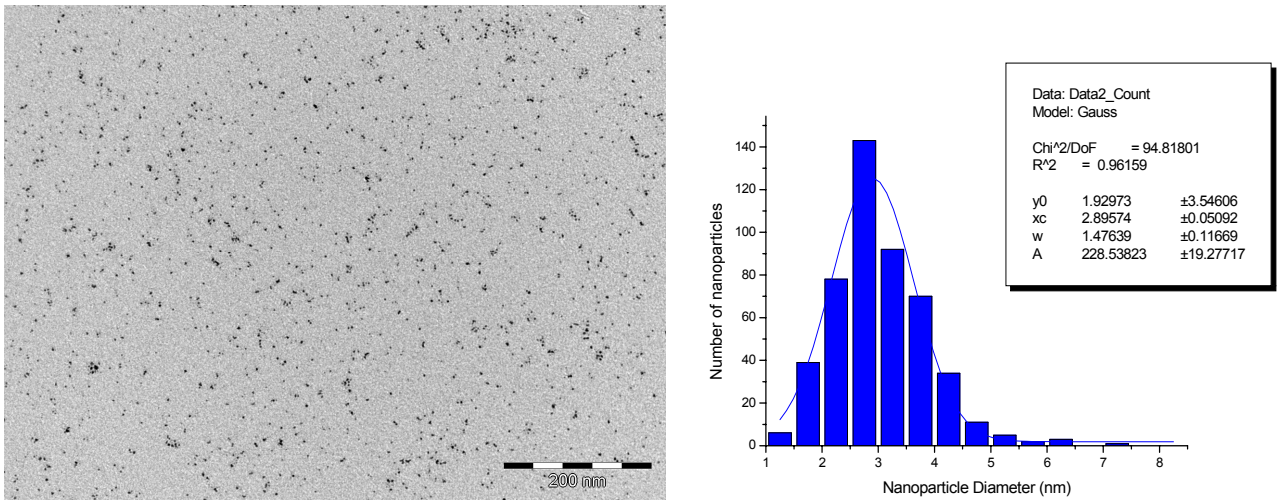


Figure 3. TEM micrograph and size histogram of Ru colloid **Ru/1b** stabilized by ligand **1b**.

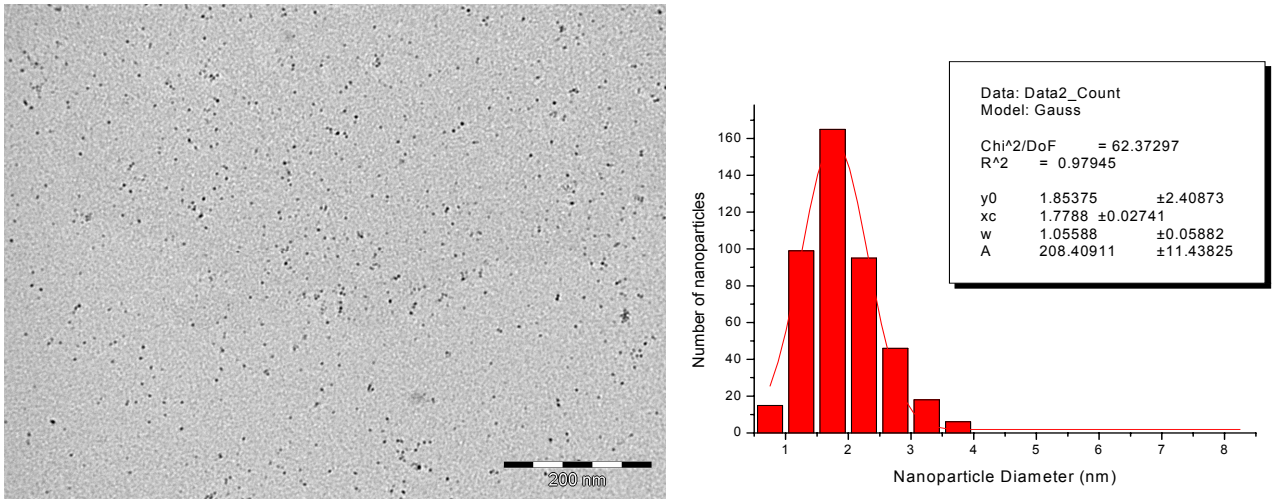


Figure 4. TEM micrograph and size histogram of Ru colloid **Ru/2b** stabilized by ligand **2b**.