† Electronic Supporting Information

Long-Chain NHC-stabilized RuNPs as Versatile Catalyst for One-pot Oxidation/Hydrogenation Reactions

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S1. General considerations and starting materials

All chemical operations were carried out using standard Schlenk tubes, Fischer–Porter bottle techniques or in a glove-box under argon atmosphere. Solvents were purified before use; THF, hexane and toluene (Sigma-Aldrich) by distillation under argon atmosphere and pentane (SDS) through filtration in the column of a purification apparatus (MBraun). Anhydrous trifluorotoluene was purchased from Sigma Aldrich and stored over molecular sieves under argon.

Ru(COD)(COT) was purchased from Nanomep Toulouse, CO from Air liquide, CO (¹³C, 99.14%) from Eurisotop, styrene (+99%) from Acros Organics. All reagents were used without purification.

ICP and Elemental Analysis. ICP and elemental analyses were performed at LCC-Toulouse on an Analyzer PERKIN ELMER 2400 série II.

Wide-angle X-ray scattering (WAXS). WAXS was performed at CEMES-CNRS. Samples were sealed in 1.5 mm diameter Lindemann glass capillaries. The samples were irradiated with graphite monochromatized molybdenum K_{α} (0.071069 nm) radiation and the X-ray intensity scattered measurements were performed using a dedicated two-axis diffractometer. Radial distribution functions (RDF) were obtained after Fourier transformation of the reduced intensity functions.

Solid state NMR (MAS-NMR). MAS-NMR analyses with and without ¹H-¹³C cross-polarization (CP) were performed at the LCC on a Bruker Avance 400WB instrument equipped with a 2.5 mm probe with the sample rotation frequency of 12 kHz. Measurements were carried out in a 2.5 mm ZrO₂ rotor.

Transmission Electron Microscopy (TEM) and High resolution TEM (HRTEM). RuNPs were observed by TEM and HRTEM after deposition of a drop of a solution of the isolated nanoparticles after dispersion in THF on a copper grid, respectively. TEM analyses were performed at the UMS-Castaing by using a JEOL JEM 1011 CX-T electron microscope operating at 100 kV with a point resolution of 4.5 Å. The approximation of the particles mean size was made through a manual analysis of enlarged micrographs by measuring a number of particles on a given grid. HRTEM observations were carried out with a JEOL JEM 2010 electron microscope working at 200 kV with a resolution point of 2.35 Å. FFT treatments have been carried out with Digital Micrograph Version 3.7.4.

Infrared spectroscopy (IR). IR Spectra were recorded on a Perkin-Elmer GX2000 spectrometer in the range 4000–400 cm-1, from samples prepared as KBr pellets.

All hydrogenation reactions were carried out in Berghof High Pressure Reactors using dihydrogen gas.

Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Strem Chemicals, Alfa Aesar, ABCR and TCI Europe and used as received unless otherwise stated.

GC/MS Spectra were recorded with an Agilent Technologies 7890A GC-system with Agilent 5975C VL MSD or 5975 inert Mass Selective Detector and a HP-5MS column (0.25 mm 30 m, Film: 0.25 mm). The methods used start with the injection temperature T0. After holding this temperature for 3 min, the column is heated to temperature T1 (ramp) and this temperature is held for an additional time t (method 50_40: T0 = 50 °C, T1 = 290 °C, ramp = 40 °C/min, t = 10 min).

S2. Synthesis of long-chain imidazolium salts

LC-IPr·HBr and LC-IMe·HI were synthesized according to the procedure described in the literature.^[1]

S3. Synthesis of ruthenium nanoparticles

*Ru@LC-IMe*_{0.3}: A Schlenk flask was charged with LC-IMe·HI (51.2 mg, 0.096 mmol, 0.3 equiv.) and KO'Bu (12 mg, 0.105 mmol, 0.33 equiv.). The solids were suspended in THF (50 mL) and stirred at r.t. for 20 h. After that the resulting suspension was filtered through dry celite (1 cm) under argon atmosphere and added to a 250 ml Fischer–Porter bottle charged with a cooled solution (-80 °C) of Ru(COD)(COT) (100 mg, 0.32 mmol, 1 equiv.) in 50 ml of THF (previously degassed by three freeze-pump cycles). The Fischer-Porter was pressurized with 3 bar of H₂, and the solution was allowed to reach the room temperature whilst the solution was stirred vigorously. A black homogeneous solution was immediately formed. The stirring was continued for 20 h at the room temperature. After that, the remaining H₂ pressure was released and the solution was evaporated until dryness. The black residue solid was re-dispersed in the minimum quantity of THF (~ 3 ml) and 150 ml of methanol was added. The resulting black precipitate was washed twice with methanol (50 mL) and dried overnight under vacuum. The size of the NPs was measured by TEM on a sample of at least 200 nanoparticles, which afforded a mean value of 1.3 (0.2) nm. Elemental analysis and ICP gave the following composition: 24.0% C, 3.9% H, 1.4% N, 37.7% Ru.

*Ru@LC-IMe*_{0.1}: A Schlenk flask was charged with LC-IMe·HI (17.0 mg, 0.032 mmol, 0.1 equiv.) and KO^tBu (4 mg, 0.034 mmol, 0.11 equiv.). The solids were suspended in THF (50 mL) and stirred at r.t. for 20 h. After that the resulting suspension was filtered through dry celite (1 cm) under argon atmosphere and added to a 250 ml Fischer–Porter bottle charged with a cooled solution (-80 °C) of Ru(COD)(COT) (100 mg, 0.32 mmol, 1 equiv.) in 50 ml of THF (previously

degassed by three freeze-pump cycles). The Fischer-Porter was pressurized with 3 bar of H_2 , and the solution was allowed to reach the room temperature whilst the solution was stirred vigorously. A black homogeneous solution was immediately formed. The stirring was continued for 20 h at the room temperature. After that, the remaining H_2 pressure was released and the solution was evaporated until dryness. The black residue solid was re-dispersed in the minimum quantity of THF (~ 3 ml) and 150 ml of methanol was added. The resulting black precipitate was washed twice with methanol (50 mL) and dried overnight under vacuum. The size of the NPs was measured by TEM on a sample of at least 200 nanoparticles, which afforded a mean value of 1.3 (0.3) nm.

*Ru@LC-IPr*_{0.3}: A Schlenk flask was charged with LC-IPr-HBr (74.6 mg, 0.096 mmol, 0.3 equiv.) and KO'Bu (12 mg, 0.105 mmol, 0.33 equiv.). The solids were suspended in THF (50 mL) and stirred at r.t. for 20 h. After that the resulting suspension was filtered through dry celite (1 cm) under argon atmosphere and added to a 250 ml Fischer–Porter bottle charged with a cooled solution (-80 °C) of Ru(COD)(COT) (100 mg, 0.32 mmol, 1 equiv.) in 50 ml of THF (previously degassed by three freeze-pump cycles). The Fischer-Porter was pressurized with 3 bar of H₂, and the solution was allowed to reach the room temperature whilst the solution was stirred vigorously. A black homogeneous solution was immediately formed. The stirring was continued for 20 h at the room temperature. After that, the remaining H₂ pressure was released and the solution was evaporated until dryness. The black residue solid was re-dispersed in the minimum quantity of THF (~ 3 ml) and 150 ml of methanol was added. The resulting black precipitate was washed twice with methanol (50 mL) and dried overnight under vacuum. The size of the NPs was measured by TEM on a sample of at least 200 nanoparticles, which afforded a mean value of 1.2 (0.2) nm. Elemental analysis and ICP gave the following composition: 34.1% C, 4.7% H, 1.4% N, 20.1% Ru.

Ru@*LC-IPr*_{0.1}: A Schlenk flask was charged with LC-IPr·HBr (24.9 mg, 0.032 mmol, 0.1 equiv.) and KO'Bu (4 mg, 0.034 mmol, 0.11 equiv.). The solids were suspended in THF (50 mL) and stirred at r.t. for 20 h. After that the resulting suspension was filtered through dry celite (1 cm) under argon atmosphere and added to a 250 ml Fischer–Porter bottle charged with a cooled solution (-80 °C) of Ru(COD)(COT) (100 mg, 0.32 mmol, 1 equiv.) in 50 ml of THF (previously degassed by three freeze-pump cycles). The Fischer-Porter was pressurized with 3 bar of H₂, and the solution was allowed to reach the room temperature whilst the solution was stirred vigorously. A black homogeneous solution was immediately formed. The stirring was continued for 20 h at the room temperature. After that, the remaining H₂ pressure was released and the solution was evaporated until dryness. The black residue solid was re-dispersed in the minimum quantity of THF (~ 3 ml) and 150 ml of methanol was added. The resulting black

precipitate was washed twice with methanol (50 mL) and dried overnight under vacuum. The size of the NPs was measured by TEM on a sample of at least 200 nanoparticles, which afforded a mean value of 1.5 (0.4) nm.

S4. Hydrogenation reactions

A screw capped glass vial was equipped with a magnetic stirring bar and was filled with NHC-RuNPs (1mg). Then the corresponding substrate (0.2 mmol) and the solvent were added (1 mL) in the glove box. The vial was placed in a stainless steel autoclave, which was carefully pressurized/depressurized with hydrogen for three times. Then the indicated pressure was adjusted and the reactor was heated during the corresponding time. Mesitylene was added after the reaction time as internal reference (28µL, 1 equiv.)

Reaction mixtures were analyzed by GC-MS. Conversions were determined by GC-FID.

S5. Oxygenation reactions

A screw capped glass vial was equipped with a magnetic stirring bar and was filled with NHC-RuNPs (1mg). Then the atmosphere was replaced by oxygen and the corresponding substrate (0.2 mmol) and the solvent were added (1 mL). The reaction mixture was stirred at r.t. during the corresponding time. Mesitylene was added after the reaction time as internal reference (28µL, 1 equiv.)

Reaction mixtures were analyzed by GC-MS. Conversions were determined by GC-FID.

S6. One-pot oxidation-hydrogenation reactions

A screw capped glass vial was equipped with a magnetic stirring bar and was filled with NHC-RuNPs (quantity indicated in Table 3). Then the atmosphere was replaced by oxygen and the substrate (0.1 mmol) and trifluorotoluene were added (0.5 mL). The reaction mixture was stirred at r.t. for 16h. In the case of entries 3 and 4 Table 3, isopropylamine (1.5 equiv) was added after this time and the resulting mixture was stirred at 25°C for 2h. Then the vial was placed in a stainless steel autoclave, which was carefully pressurized/depressurized with hydrogen for three times. Then a pressure of 5 bar was adjusted and the reactor was heated at the corresponding temperature during the corresponding time.

Reaction mixtures were analyzed by GC-MS. Conversions were determined by GC-FID.

S7. Synthesis and analytical data of oxidation-hydrogenation reaction product references

Compounds 19, 20 and 21 are commercially available.

Compounds **22** and **23** were prepared by a modified procedure according to: J. Med. Chem. **2014**, *57*, 2845 - 2850.

N-benzylpropan-2-amine 22



Benzylamine (109 µL, 1.00 mmol, 1 eq), acetone (81 µL, 1.00 mmol, 1 eq) and methanol (2 mL) were added to a Schlenk-flask and stirred at RT overnight. Sodium borohydride (76 mg, 2.00 mmol, 2 eq) was added and the reaction mixture was stirred for 5 h open to air. The reaction was quenched by addition of HCI (2 M) maintain a pH of 1. The aqueous layer was extracted with diethyl ether (3 x 5 mL) and 3 M NaOH was added resulting in a pH of 14. The aqueous layer was extracted with diethyl ether (3 x 5 mL) and 3 M NaOH was added resulting in a pH of 14. The aqueous layer was extracted with diethyl ether (3 x 5 mL), the combined organic layers were dried with MgSO₄ and concentrated to give **22** as a white solid (91.5 mg, 0.61 mmol, 61%). ¹H-NMR (300 MHz, CDCl₃) δ [ppm] = 7.34 - 7.30 (m, 4H), 7.26 - 7.21 (m, 1H), 3.78 (s, 2H), 2.86 (p, J = 6.2 Hz, 1H), 1.40 - 1.18 (bs, 1 H), 1.10 (d, J = 6.2 Hz, 6H); ¹³C-NMR (75 MHz, CDCl₃) δ [ppm] = 141.0, 128.7, 128.6, 128.3, 127.2, 127.0, 51.8, 48.2, 23.1; ESI-MS: calculated [C₁₀H₁₅NH]⁺ 150.1277, found 150.1280.



¹H-NMR spectrum of **22**



240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)

N-(cyclohexylmethyl)propan-2-amine 23

N H

Cyclohexylmethylamine (132 µL, 1.00 mmol, 1 eq), acetone (81 µL, 1.00 mmol, 1 eq) and methanol (2 mL) were added to a Schlenk-flask and stirred at RT overnight. Sodium borohydride (76 mg, 2.00 mmol, 2 eq) was added and the reaction mixture was stirred for 3.5 h open to air. The reaction was quenched by addition of HCI (2 M) maintain a pH of 1. The aqueous layer was extracted with diethyl ether (3 x 5 mL) and 3 M NaOH was added resulting in a pH of 14. The aqueous layer was extracted with diethyl ether (3 x 5 mL) and 3 M NaOH was added resulting organic layers were dried with MgSO₄. Because no full conversion was achieved the product was purified by flash column chromatography (*n*-pentane/Et₂O = 5/2) giving **23** as a white solid (35.0 mg, 0.23 mmol, 23%).¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 2.78 - 2.65 (m, 1H), 2.41 (d, J = 6.7 Hz, 2H), 1.77 - 1.61 (m, 5H), 1.47 - 1.36 (m, 1H), 1.30 - 1.11 (m, 4H), 1.04 (d, J = 6.3 Hz, 6H), 0.95 - 0.83 (m, 2H); ¹³C-NMR (75 MHz, CDCl₃) δ [ppm] = 54.5, 48.7, 38.3, 31.8, 26.9, 26.3, 23.3; ESI-MS: calculated [C₁₀H₂₁NH]⁺ 156.1747, found 156.1761; R_f (*n*-pentane/Et₂O = 5/2): 0.1.



¹³C-NMR spectrum of 23

 $\begin{array}{c} 54.5\\ - & 48.9\\ - & 31.7\\ - & 26.9\\ - & 23.2\\ - & 23.2\\ - & - \end{array}$





S8. GC-MS retention times of 3-23

Compound	GC-MS	Compound	GC-MS
	retention time		retention time
	(min)		(min)
3	5.942	14	5.288
4	5.842	15	6.751
5	8.304	16	6.827
6	7.849	17	5.631
7	7.858	18	5.455
8	7.800	19	6.335
9	4.957	20	6.510
10	4.515	21	6.639
11	8.708	22	6.434
12	8.286	23	6.270
13	5.740		

S9. Surfaces studies of RuNPs through coordination of CO and ¹³CO

For CO coordination studies, RuNPs were introduced in a Fischer-Porter bottle and were pressurized with 3 bar of H_2 for 20h to avoid the presence of oxygen on the surface. After this period of time, the dihydrogen gas was evacuated under vacuum for 15 min. The Fischer-Porter bottle was further pressurized with 1 bar of CO/¹³CO for 24 h. Then, the gas was evacuated under vacuum for 5 min.

¹³C solid state NMR was recorded after transfer of the sample into a NMR rotor and FT-IR spectra were recorded from samples prepared as KBr pellets.

S10. HRTEM data of RuNPs



Figure S1. HRTEM micrographs of Ru@LC-IMe_{0,3} **1a** (left, right bottom) and the Fourier Transform Analysis (right top) with planar reflections. Fourier transform analysis applied to this image presents reflections to (100), (002) and (101) atomic planes.



Figure S2. HRTEM micrographs of Ru@LC-IPr_{0,3} **2a** (left, right bottom) and the Fourier Transform Analysis (right top) with planar reflections. Fourier transform analysis applied to this image presents reflections to (101), (101) and (002) atomic planes.

S11. WAXS data of RuNPs

Wide-Angle X-ray Scattering (WAXS) of $Ru@LC-IMe_{0,3}$ **1a** revealed metallic NPs with a compact structure (hcp) and a coherence length around 1.3 nm (Figure S5, red). After exposure to air for 3 days at r.t., **1a** were essentially oxidized, observing a pattern in agreement with amorphous RuO_2 (Figure S5, green).



Figure S3. WAXS analysis of $Ru@LC-IMe_{0,3}$ 1a before (red) and after (green) exposure to air (3 days; r.t.).

WAXS of Ru@LC-IPr_{0,3} **2a** shows crystalline RuNPs with hcp structure and coherence length around 1.3 nm. When Ru@LC-IPr_{0,3} **2a** were exposed to open air during 3 days at r.t., the NPs were practically oxidized, the pattern fitting almost perfectly with RuO₂ (see SI, Figure S6). As a rule, WAXS analyses of Ru@LC-NHCs showed metallic ruthenium NPs with an hcp structure which after exposure to open air (3 days, r.t.) were practically oxidized. Their RDFs display clear oxidation signs: a peak at short distance, about 0.195 nm, attributed to Ru-O and another at longer distance (0.38 nm) due to Ru-O-Ru. But we can also find a persistent peak at 0.268 nm which corresponds to the metallic bond length in ruthenium, indicating that even after three days of exposure to air we have only a partial oxidation of the NPs. The oxide is very amorphous with a short coherence length mainly related to residual metallic ruthenium. We can roughly estimate a metallic core of 0.7 nm for Ru@LC-IMe_{0.3} **1a** and some persistent clusters of a few atoms in Ru@LC-IPr_{0.3} **2a**.



Figure S4. WAXS analysis of Ru@LC-IPr_{0,3} **2a** before (red) and after (green) exposure to air (3 days; r.t.).



S12. IR data of RuNPs

Figure S5. IR spectra registered for the $Ru@LC-IMe_{0.3}$ **1a** before (blue) and after (red) adsorption of CO (1 bar, r.t., 20 h).



Figure S6. IR spectra registered for the Ru@LC-IPr_{0.3} **2a** before (blue) and after (red) adsorption of CO (1 bar, r.t., 20 h).

S13. NMR data of RuNPs



Figure S7. ¹³C MAS (top) and CP-MAS (bottom) NMR spectra of Ru@LC-IMe_{0.3}**1a**. The signal with asterisk corresponds to grease.



Figure S8. ¹³C MAS (top) and CP-MAS (bottom) NMR spectra of Ru@LC-IPr_{0.3} **2a**. The signal with asterisk corresponds to grease.



Figure S9: ¹³C CP-MAS NMR spectra of Ru@LC-IMe_{0.3} **1a** (top) and Ru@LC-IPr_{0.3} **2a** (bottom) NPs after exposure to ¹³CO (1 bar, 20 h, at r.t.).

S14. Oxidation stability experiments

Successive oxidation reactions:





 $Ru@LC-IMe_{0.3}$: Conv = 64% $Ru@LC-IPr_{0.3}$: Conv = 85%



Ru@LC-IM_{e0.3}: Conv = 48% Ru@LC-IPr_{0.3}: Conv = 52%

Scheme S1. Stability test of Ru@LC-IMe_{0.3} and Ru@LC-IPr_{0.3}.

A screw capped glass vial was equipped with a magnetic stirring bar and was filled with NHC-RuNPs (1mg). Then the atmosphere was replaced by oxygen and benzyl alcohol (21 μ L, 0.2 mmol, 1 equiv.) and benzotrifluoride (1 mL) were added. The reaction mixture was stirred at r.t. for 16 h. Mesitylene was added as internal reference (28 μ L, 1 equiv.) and the conversion of benzaldehyde was determined by GC-FID. Geraniol (35 μ L, 0.2 mmol, 1 equiv.) was added, the atmosphere replaced by fresh oxygen and the reaction mixture stirred for additional 24 h at r.t. The conversions of benzaldehyde and geraniol were determined by GC-FID.

"Post-mortem" TEM and HRTEM analysis:

For these studies, NPs used as catalysts in the oxidation of benzyl alcohol **16** into benzaldehyde **17** (Table 2, entries 1 and 3) were purified and re-dispersed in THF. A drop of this colloidal solution was deposited on a copper grid and analyzed by TEM and HRTEM.



Figure S10. TEM micrographs and the corresponding size histograms of Ru@LC-IPr_{0.3} (left) and Ru@LC-IMe_{0.3} (right) after oxidation of benzyl alcohol (Table 3, entries 1 and 3).



Figure S11. HRTEM micrographs of Ru@LC-IPr_{0.3} (left) and Ru@LC-IMe_{0.3} (right) after oxidation of benzyl alcohol (Table 3, entries 1 and 3).

^[1] C. Richter, K. Schaepe, F. Glorius and B. J. Ravoo, *Chem. Comm.* 2014, **50**, 3204-3207.