

## † Electronic Supporting Information

### **Betaine adduct of N-heterocyclic carbene and carbodiimide, an efficient ligand to produce ultra-small ruthenium nanoparticles**

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## **EXPERIMENTAL SECTION**

### **General and starting materials**

All chemical operations were carried out using standard Schlenk tube or Fischer–Porter bottle techniques or in a glove-box under argon atmosphere. Solvents were purified before use; THF (Sigma-Aldrich) by distillation under argon atmosphere with sodium/benzophenone and pentane (SDS) through filtration in the column of a purification apparatus (MBraun).

Ru(COD)(COT) was purchased from Nanomeps-Toulouse, CO from Air liquide, CO (<sup>13</sup>C, 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 the “Laboratoire de Chimie de Coordination” in 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<sub>α</sub> (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  $^1\text{H}$ - $^{13}\text{C}$  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  $\text{ZrO}_2$  rotor.

*Transmission electron microscopy (TEM).* TEM observation were performed at the "Service Commun de Microscopie Electronique de l'Université Paul Sabatier (TEMSCAN)" on a JEOL JEM 1400 CX-T electron microscope operating at 120 kV. TEM grids were prepared by drop-casting of the crude colloidal solution in THF on a holey carbon-coated copper grid. Size histograms have been built with the help of the software ImageJ.

*ElectroSpray Ionization Mass Spectrometry (ESI-MS).* ESI-MS analysis were carried out at the Service Commun de Spectrometrie de Masse de l'Université Paul Sabatier at Toulouse in a AB Sciex Q TRAP 2000 spectrometer, with electrospray in positive mode and direct analysis. Sample were diluted in methanol.

*Gas chromatography (G.C.).* G.C. was performed using a HP 5890 Series II Gas Chromatograph with a SGE BP1 non polar 100% dimethyl polysiloxane capillary column of 50 m x 0.32 mm x 0.25  $\mu\text{m}$ . The method used for the quantification of hydrides consists of 15 min. at 40 °C and a 3 ramp of 8 °C/min until 250 °C. The method used for styrene hydrogenation experiments consists of 3 min at 80 °C and a ramp of 8 °C/min until 210 °C.

### **Synthesis of 1,3-dicyclohexylimidazolidene and di-*p*-tolylcarbodiimide (ICy·(*p*-tol)NCN)**

4 mL of a 1M solution of KO<sup>t</sup>Bu in 30 mL THF were added dropwise to a solution of 1.26 g (4 mmol) of 1,3-dicyclohexylimidazolium bromide in 20 mL of the same solvent stirred at -80 °C. The cooling bath was removed and the stirring was continued for *ca.* 30 min while the mixture warmed to the room temperature. The flask was cooled again to -80 °C, and di-*p*-tolylcarbodiimide (0.889 g, 4 mmol) dissolved in 10 mL of THF was added dropwise. The mixture was allowed to warm again to the room temperature, taken to dryness and extracted with 2 x 20 mL of  $\text{CH}_2\text{Cl}_2$ . The extract was taken to dryness, and the residue was washed with hexane (3 x 10 mL) and dried under vacuum. Bright yellow microcrystalline solid. Yield, 1.507 g, 83 %.

$^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C):  $\delta$  1.15 (m, 2 H, Cy); 1.35 (m, 8 H, Cy); 1.69 (m, 2 H, Cy); 1.83 (m, 6 H, Cy); 1.85 (br m, 2 H, Cy); 2.24 (s, 6 H, *p*-Me); 4.55 (m, 2H, Cy-CH); 6.89 (br s, 4H, *p*-Tol); 6.95 (s, 2H, Imdz).  $^{13}\text{C}\{^1\text{H}\}$  (75 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C):  $\delta$  20.7 (*p*- $\text{CH}_3$ ); 25.3 ( $\text{CH}_2$  Cy); 25.7 ( $\text{CH}_2$  Cy); 33.4 (4- $\text{CH}_2$  Cy); 58.4 (CH, Cy); 116.3 (CH Imdz); 122.9 (br s, *o*-CH *p*-Tol); 128.6 (*p*-C *p*-Tol); 129.1 (*o*-CH *p*-Tol); 145.1 (*ipso*-C *p*-Tol); 146.7 (Cq Imdz); 150.7 ( $\text{CN}_2$ ). ESI-MS (MeOH)  $m/Z$  = 455.3 ( $\text{HM}^+$ ). IR (Nujol Mull,  $\text{cm}^{-1}$ ): 1609 (m,  $\nu_{\text{CC arom}}$ ); 1503 (st,  $\nu_{\text{CN CNN}}$ ); 1494 (st, Imdz).

### Synthesis of ruthenium nanoparticles

*Ru-ICy<sup>·(p-tol)</sup>NCN<sub>0,1</sub>*: A 250 ml Fischer–Porter bottle provided with a stirring bar was charged with Ru(COD)(COT) (150 mg, 0.48 mmol) and 75 ml of THF, previously degassed by three freeze-pump cycles. The resulting yellow solution was cooled at -80°C and a THF solution of (75 ml) containing 0.1 equiv. of ICy<sup>·(p-tol)</sup>NCN betaine adduct (21.9 mg, 0.048 mmol) was added. The Fischer-Porter was then pressurized with 3 bar of H<sub>2</sub>, and the solution was allowed to reach the room temperature under vigorous stirring. A black homogeneous solution was immediately formed. The stirring was continued for 20 h at r.t. After that period of time, the remaining H<sub>2</sub> pressure was released, the solution was transferred to a Schlenk tube and concentrated by to 10 ml, before adding 50 ml of pentane. The resulting black precipitate was washed twice with pentane (50 mL) and dried overnight under vacuum. The size of the NPs was measured by TEM on a sample of at least 100 nanoparticles, which afforded a mean value of 1.3 (0.2) nm. [ICy<sup>·(p-tol)</sup>NCN]/[Ru] = 0.1. Surface Ru atoms = 63; Core atoms: 29; % Surface atoms = 69 %

*Ru-ICy<sup>·(p-tol)</sup>NCN<sub>0,2</sub>*: A 250 ml Fischer–Porter bottle provided with a stirring bar was charged with Ru(COD)(COT) (150 mg, 0.48 mmol) and 75 ml of THF, previously degassed by three freeze-pump cycles. The resulting yellow solution was cooled at -80°C and a THF solution of (75 ml) containing 0.2 equiv. of ICy<sup>·(p-tol)</sup>NCN betaine adduct (43.8 mg, 0.096 mmol) was added. The Fischer-Porter was then pressurized with 3 bar of H<sub>2</sub>, and the solution was allowed to reach the room temperature under vigorous stirring. A black homogeneous solution was immediately formed. The stirring was continued for 20 h at r.t. After that period of time, the remaining H<sub>2</sub> pressure was released, the solution was transferred to a Schlenk tube and concentrated by to 10 ml, before adding 50 ml of pentane. The resulting black precipitate was washed twice with pentane (50 mL) and dried overnight under vacuum. The size of the NPs was measured by TEM on a sample of at least 100 nanoparticles, which afforded a mean value of 0.1(0.2) nm. [ICy<sup>·(p-tol)</sup>NCN]/[Ru] = 0.2. Surface Ru atoms = 43; Core atoms: 12; % Surface atoms = 78%.

### Reaction of Ru-ICy<sup>·(p-tol)</sup>NCN<sub>0,1</sub> and octanethiol.

0,1 ml of octanethiol (10 equiv.) was added to a suspension of 20 mg of Ru-ICy<sup>·(p-tol)</sup>NCN<sub>0,1</sub> in 5 ml C<sub>6</sub>D<sub>6</sub> and heated at 65 °C. <sup>1</sup>H and <sup>13</sup>C NMR spectrums of the crude of the reaction were registered at different times (t = 0, 4h, 24h).

### Oxidation of Ru-ICy<sup>·(p-tol)</sup>NCN<sub>0,2</sub>.

A suspension of 20 mg of Ru-ICy<sup>·(p-tol)</sup>NCN<sub>0,2</sub> in 25 ml EtOH was refluxed under air at 80 °C. After 4 hours an aliquot was taken and analyzed by ElectroSpray Ionization Mass Spectrometry (ESI-MS).

### Catalytic styrene hydrogenation with Ru NPs.

Ru-ICy-(p-tol)NCN (7-9 mg), corresponding to 0.045 mmol of ruthenium were introduced into a Fischer–Porter bottle under argon. Then, 1 ml of styrene (9.5 mmol) and 5 ml THF were added, and the mixture was pressurized with 3 bar H<sub>2</sub>. The reaction mixture was stirred at room temperature (25 °C) and aliquots were taken at different reaction times and analyzed by gas chromatography.

### Quantification of Hydrides at the Surface of Ruthenium Nanoparticles.

The general procedure for the preparation of reaction mixtures for the quantification of hydrogen atoms adsorbed onto the surface of Ru nanoparticles by CPG analyses was carried out following a previously described procedure. Each colloidal solution has been prepared in THF. On each fresh colloidal solution, five cycles of vacuum/argon were performed in order to eliminate the H<sub>2</sub> solved into the solvent. Then, 5 equivalents of 2-norbornene, were added. Samples were regularly taken from the solutions (after 2, 18, and 24 h) for CPG analyses and estimation of the olefins conversion into alkanes (Table S1).

**Table S1.** <sup>a</sup> Hydrogenation of 2-norbornene with Ru-ICy-(p-tol)NCN<sub>0,1</sub> and Ru-ICy-(p-tol)NCN<sub>0,2</sub>.  
<sup>b</sup> Quantification of hydrides

Catalysts	Reaction time (hours)				Quantification of hydrides
	0	2	18	24	
Ru-ICy-(p-tol)NCN <sub>0,1</sub>	100:0	99,5:0,5	99,5:0,5	99,5:0,5	0
Ru-ICy-(p-tol)NCN <sub>0,2</sub>	100:0	92:8	92:8	90:10	0,6

<sup>a</sup> Products ratio in % to A:B (A = 2-norbornene; B = norbornane). Catalytic conditions: T<sup>a</sup> = 25 °C; Ratio Ru/2-norbornene = 1:5; [Ru] ~ 0.05 mmol; Conversion determined by G.C. <sup>b</sup> We considered nanoparticles mean sizes and surface ruthenium atom contents as following: Ru-ICy-(p-tol)NCN<sub>0,1</sub> NPs (mean size: 1.3 nm; 69% surface atoms) and for Ru-ICy-(p-tol)NCN<sub>0,2</sub> NPs (mean size: 0.1 nm; 78% surface atoms)

To get nanoparticles-free solutions, filtration of the samples was realized through an Al<sub>2</sub>O<sub>3</sub> pad. The systems used for these measurements were: (a) Ru-ICy-(p-tol)NCN<sub>0,1</sub>; (b) Ru-ICy-(p-tol)NCN<sub>0,2</sub>

## COMPLEMENTARY FIGURES

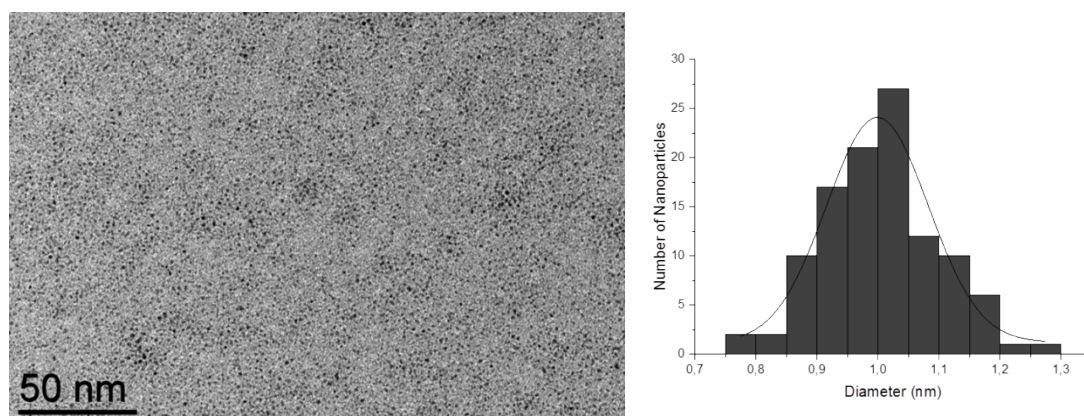


Figure S1. TEM image and the corresponding size histogram of Ru-ICy-(p-tol)NCN<sub>0.5</sub>.

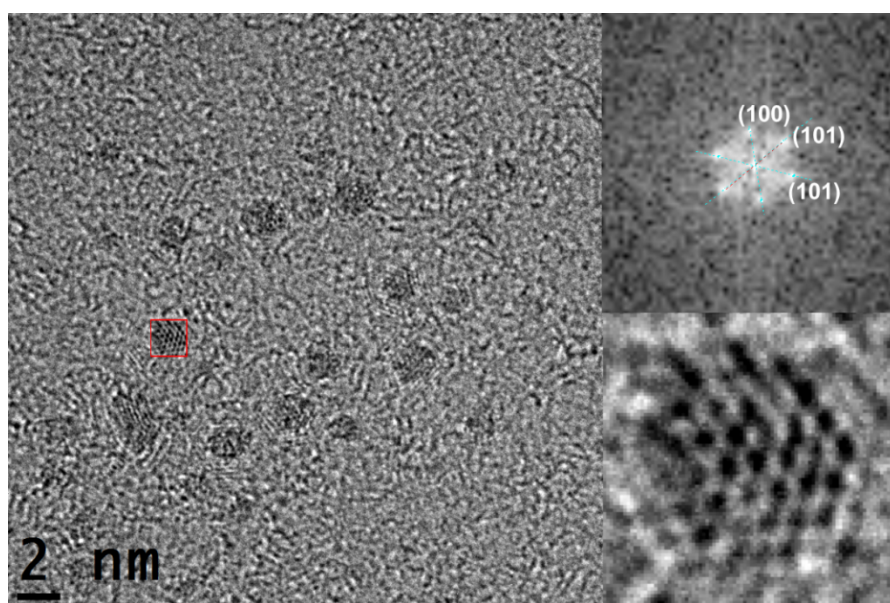


Figure S2. HRTEM image of Ru-ICy-(p-tol)NCN<sub>0.1</sub> (left, right bottom) and the Fourier Transform Analysis (right, top) with planar reflections.

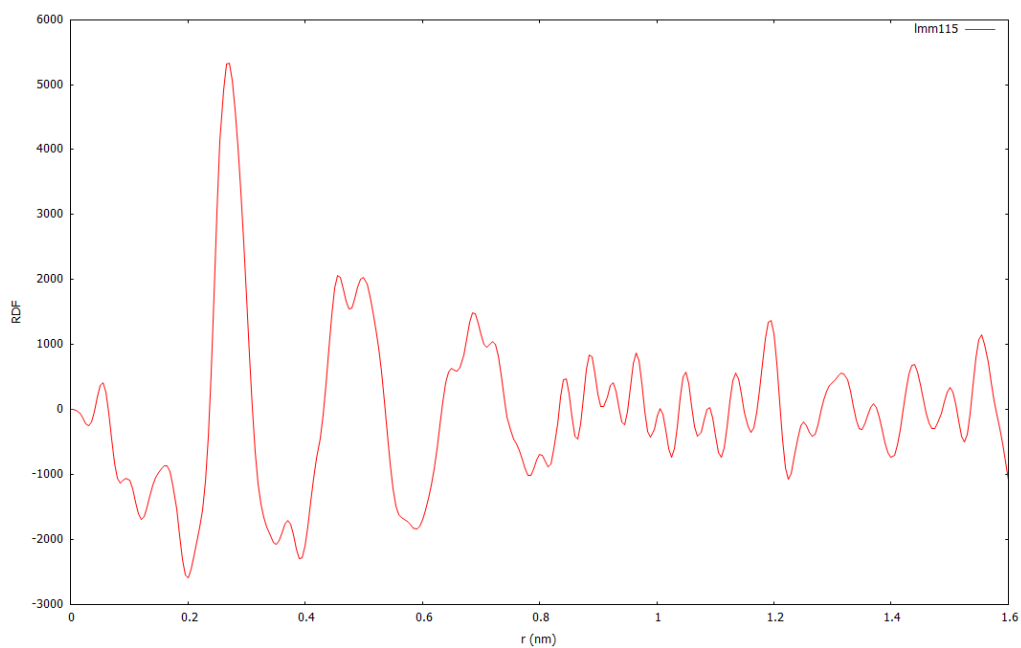


Figure S3. WAXS analysis of Ru-ICy-(p-tol)NCN<sub>0.1</sub>.

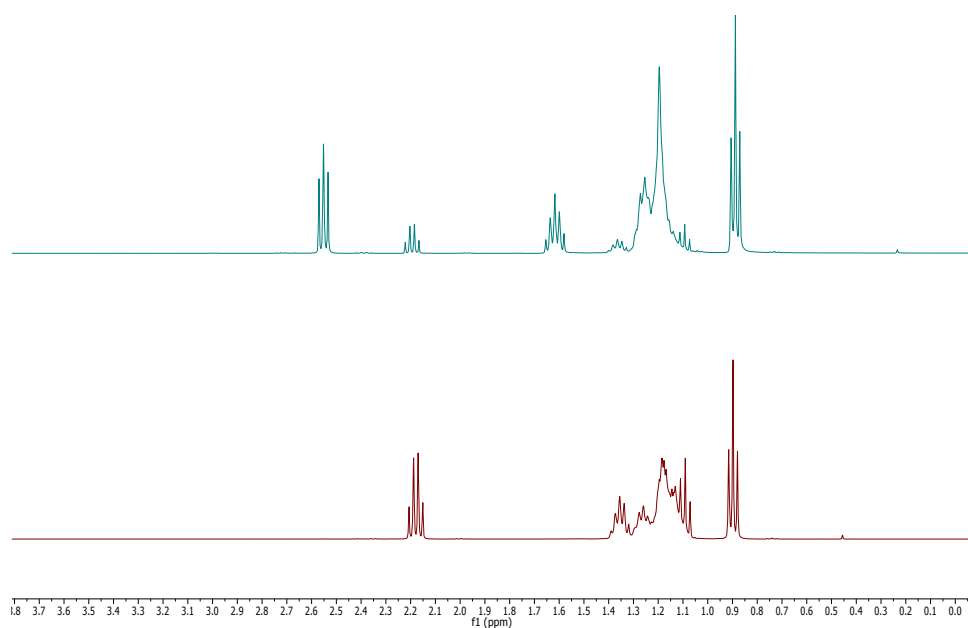


Figure S4. <sup>1</sup>H NMR spectra of Ru-ICy-(p-tol)NCN<sub>0.1</sub> NPs obtained after reaction with 10 equiv. of octanethiol at 65 °C. Bottom: t = 0h. Up: t = 24 h.

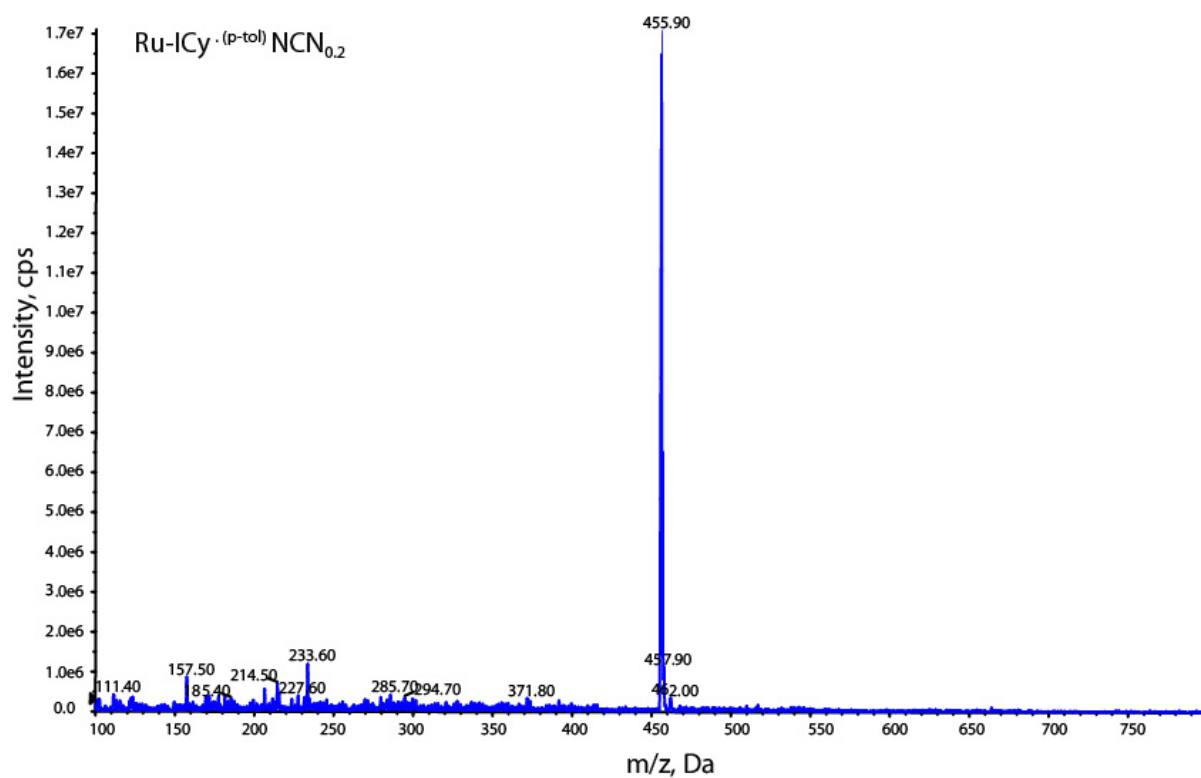
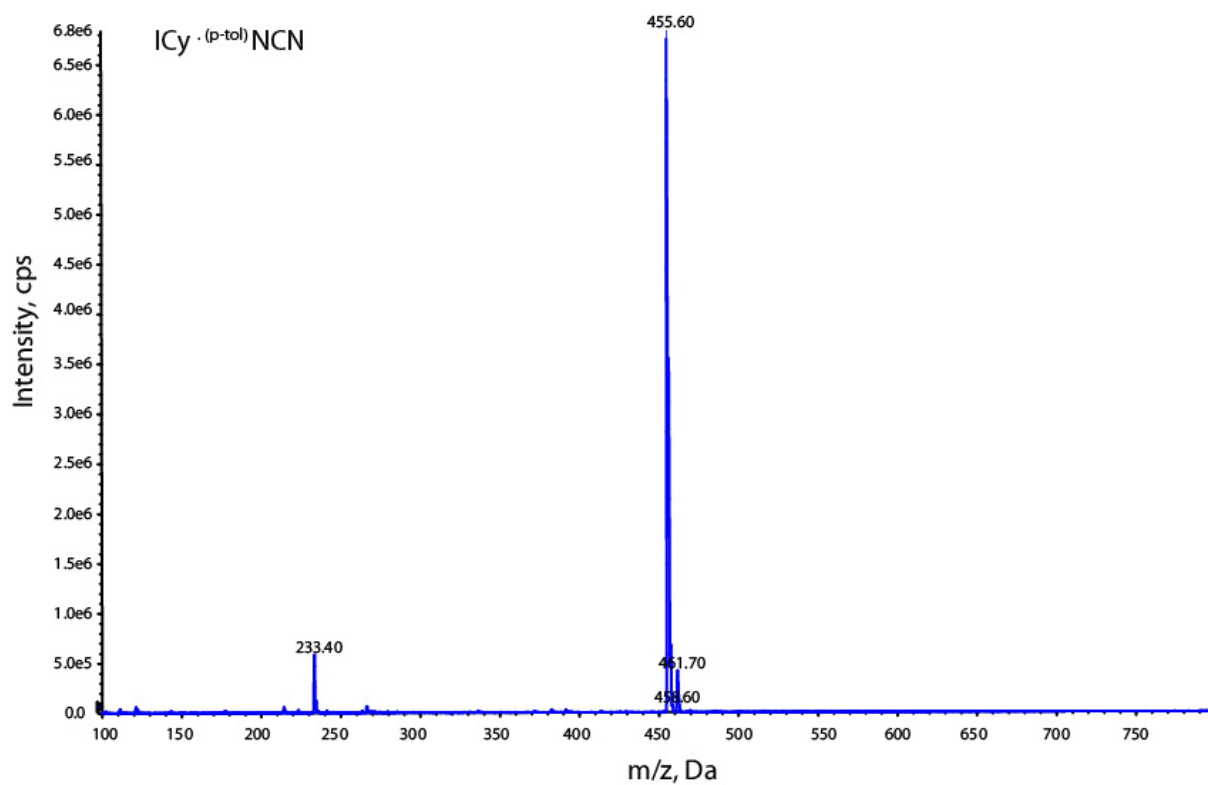


Figure S5. Top: ESI-MS spectrum of a sample of  $\text{ICy} \cdot (\text{p-tol})\text{NCN}$  in EtOH. Bottom: ESI-MS spectrum corresponding to  $\text{Ru-ICy} \cdot (\text{p-tol})\text{NCN}_{0.2}$  after oxidation (4h of reflux under air at  $80^\circ\text{C}$  in EtOH).

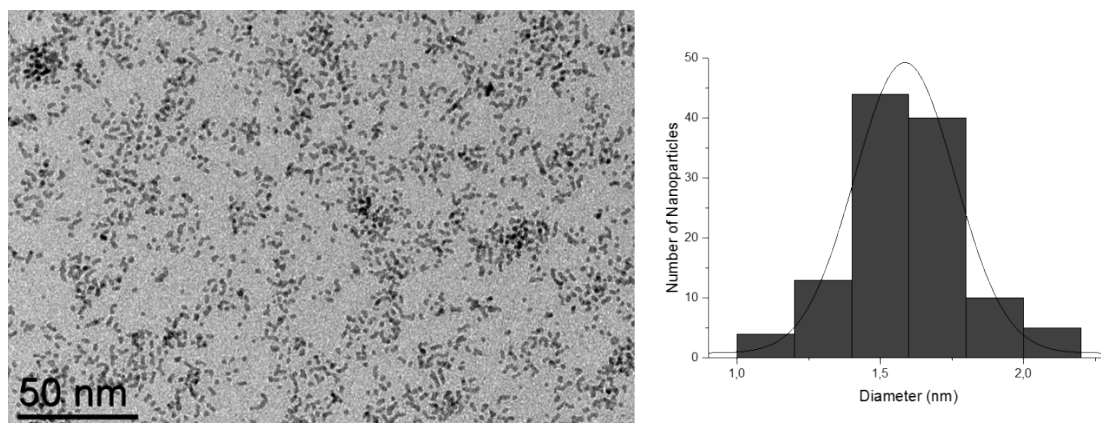


Figure S6. TEM image and the corresponding size histogram of Ru-(p-tol)NCN<sub>0.2</sub>.

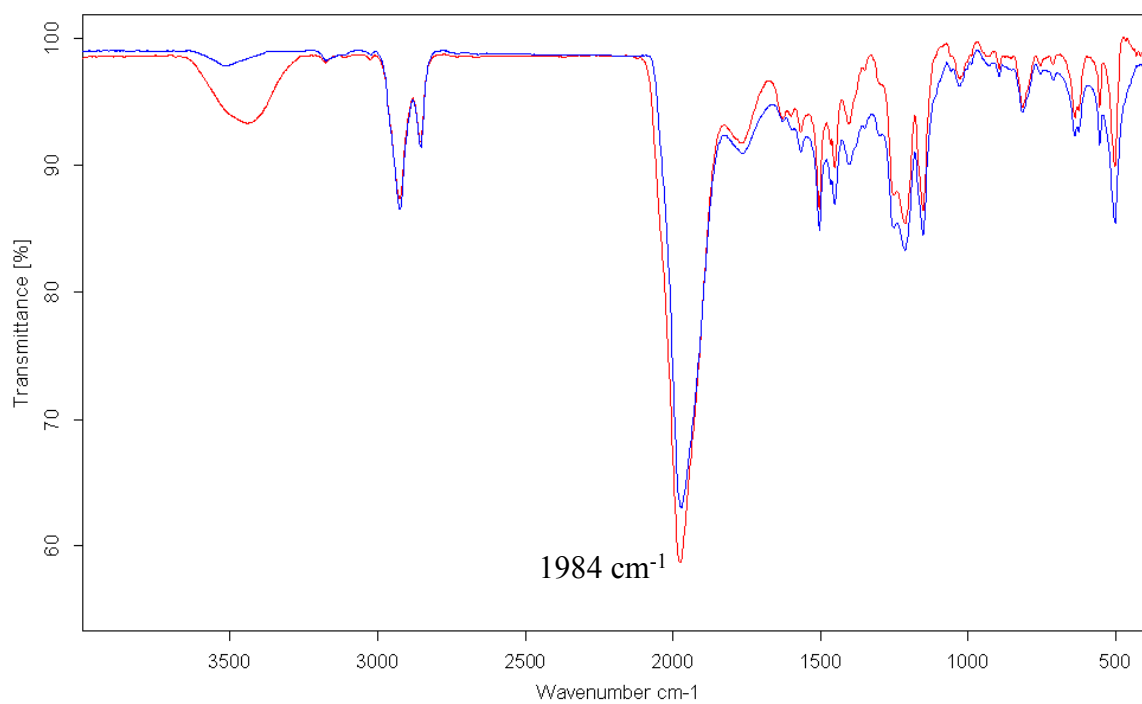


Figure S7. FT-IR spectra of a sample of ICy-(p-tol)NCN<sub>0.1</sub> before (blue) and after (red) exposure to CO (1 bar, 20h, at r.t.).



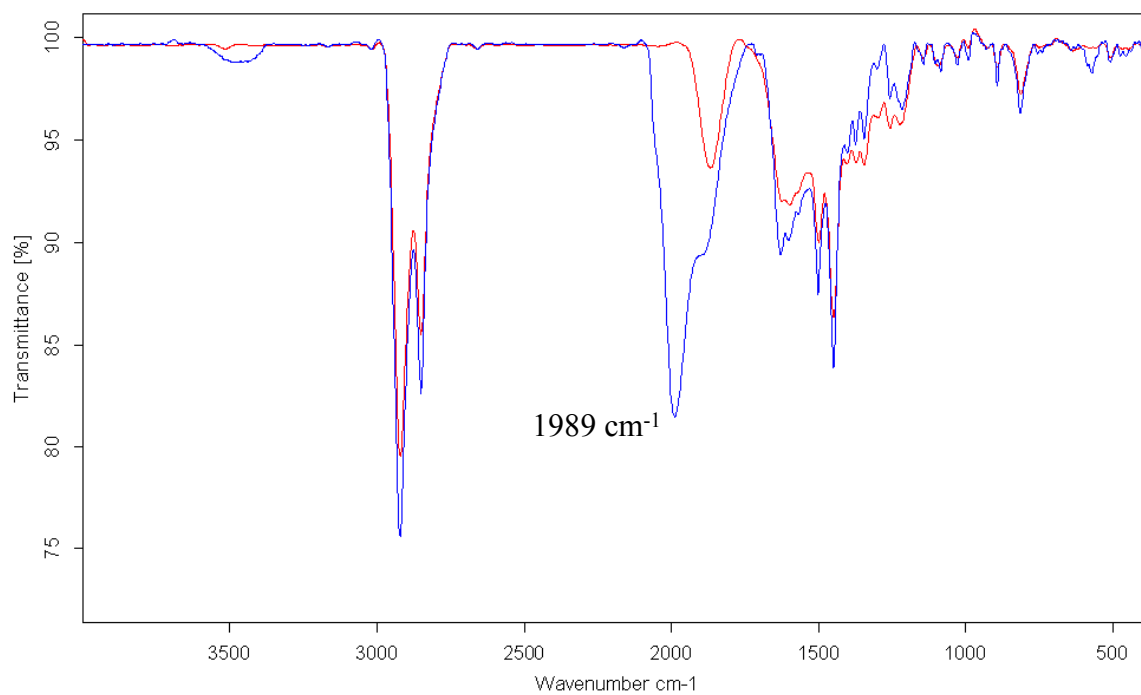


Figure S8. FT-IR spectra of a sample of ICy-(p-tol)NCN<sub>0.2</sub> before (blue) and after (red) exposure to CO (1 bar, 20h, at r.t.).

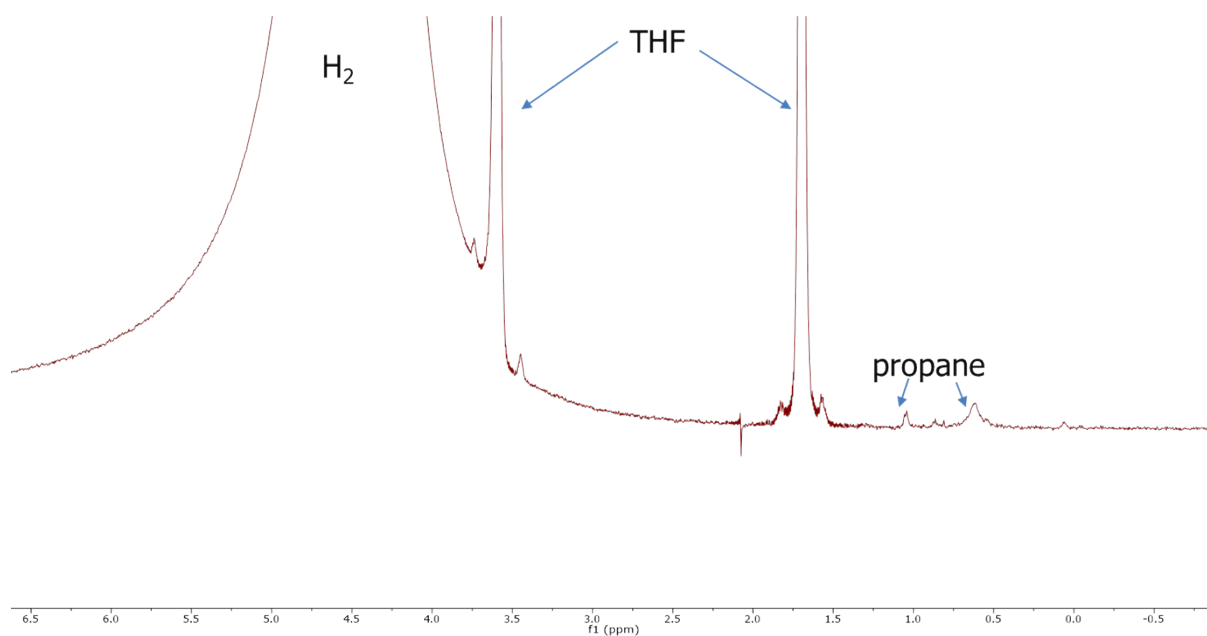


Figure S9. Gas phase NMR after synthesis of Ru-ICy-(p-tol)NCN<sub>0.1</sub>.

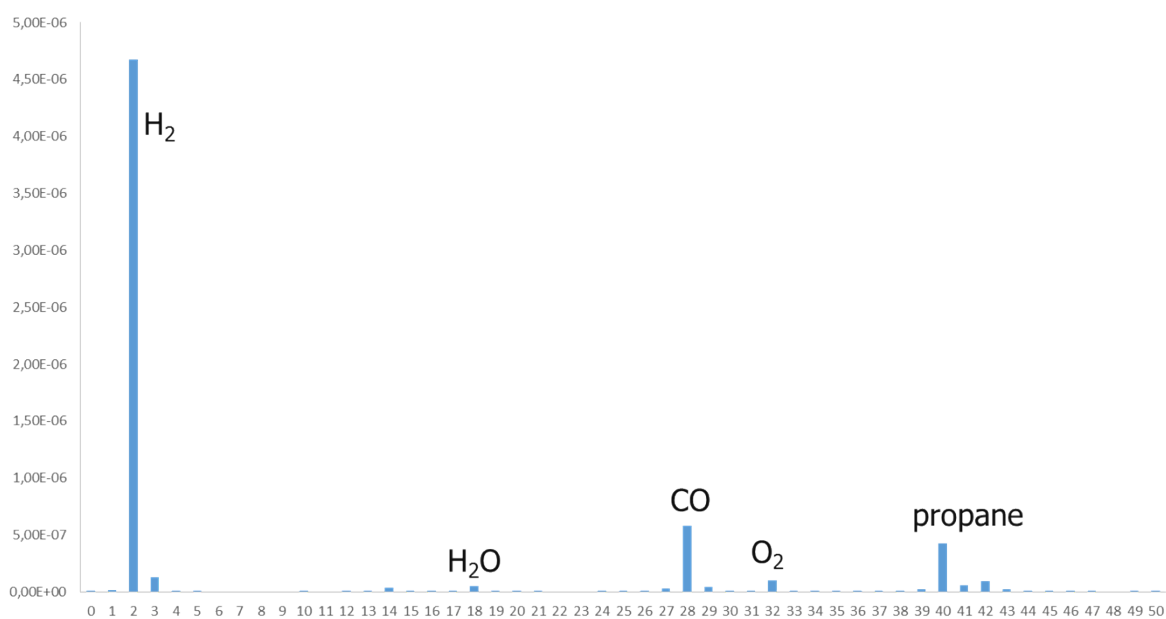


Figure S10. Analysis by MS of the gas phase after synthesis of Ru-ICy·(p-tol)NCN<sub>0.1</sub>.

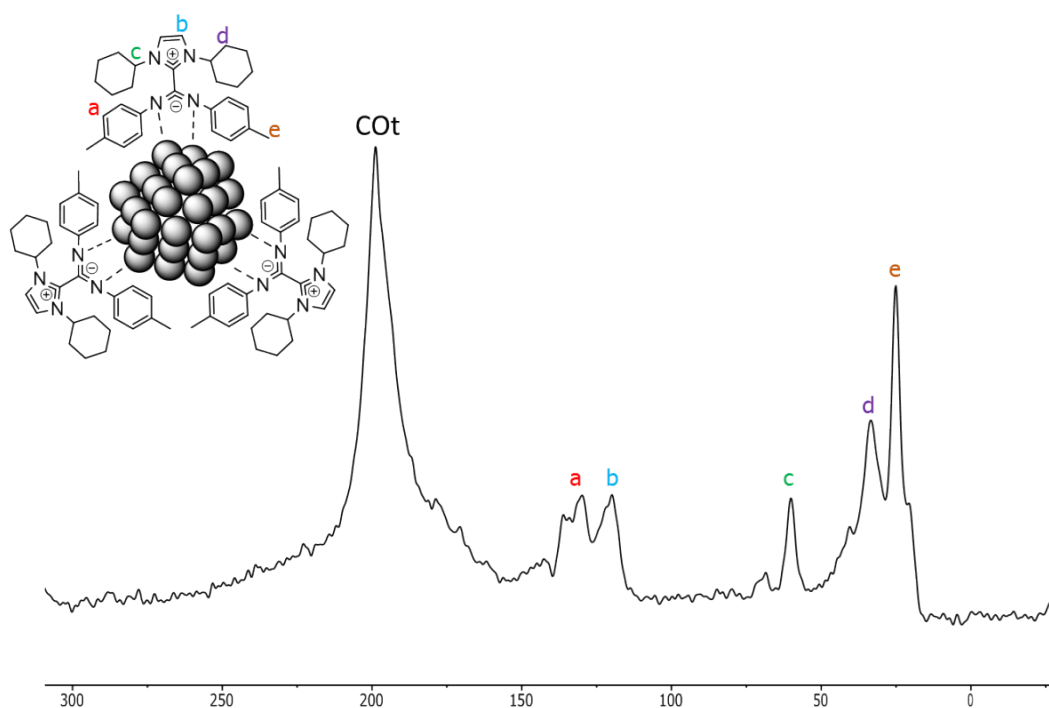


Figure S11. <sup>13</sup>C CP- MAS <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of Ru-ICy·(p-tol)NCN<sub>0.1</sub> after exposure to <sup>13</sup>CO (1 bar, 20h, at r.t.).

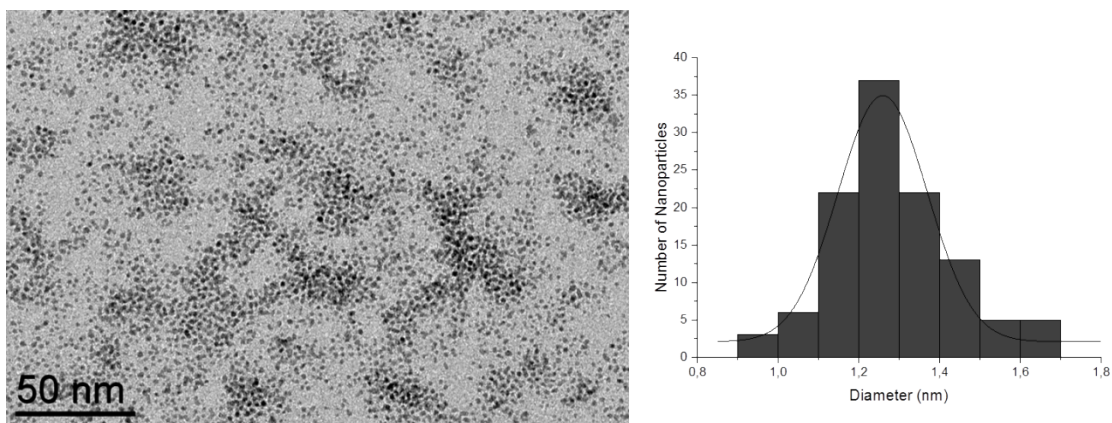


Figure S12. TEM image and the corresponding size histogram of Ru-ICy-(p-tol)NCN<sub>0.1</sub>.

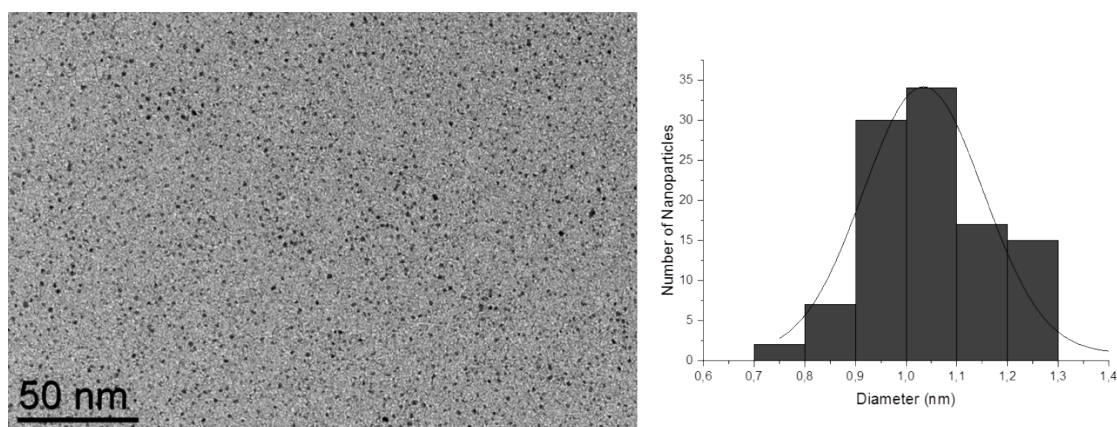


Figure S13. TEM image and the corresponding size histogram of Ru-ICy-(p-tol)NCN<sub>0.2</sub>.