Electronic Supporting Information

When organophosphorus ruthenium complexes covalently bind to ruthenium nanoparticles to form nanoscale hybrid materials

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1. Experimental section

1.1. Materials.

All operations for the synthesis of the [RuPMe]⁺-stabilized ruthenium NPs were performed using standard Schlenk tubes, Fisher–Porter bottle techniques or in a glovebox (MBraun) under an argon atmosphere (Air Liquide, classe 2, U 1006).

Tetrahydrofurane (THF; CarloErba) was purified by filtration on adequate column in a purification apparatus (MBraun) and degassed before use according to a freeze–pump–thaw process. Acetonitrile (CH₃CN; CarloErba) and acetone (CarloErba) were purified by distillation on P_2O_5 and MgSO₄, respectively.

(1,5-cyclooctadiene)(1,3,5-cyclooctatriene)ruthenium(0), [Ru(cod)(cot)], was purchased from Nanomeps-Toulouse, *Cis*-dichlorobis(2,2)-bipyridine)ruthenium(II), [Ru(bpy)₂Cl₂], and methyldiphenylphosphine, Ph₂PCH₃, from Aldrich, Thallium(I) hexafluorophosphate, TIPF₆, from Alfa Aesar.

Hydrogen was purchased from Air Liquide (Alphagaz), ¹³CO from Eurisotop.

Deuterated solvents (CD₃CN) for NMR studies were purchased from Eurisotop and stored on activated molecular sieves inside a glove box.

1.2. Sample Synthesis.

Synthesis of [(bpy)₂Ru(Ph₂PMe)Cl]⁺PF₆ named as [RuPMe]⁺

A solution of 10 mL of TIPF₆, (83,8 mg; 0,24 mmol) in acetone was added to cis-[Ru(bpy)₂Cl₂], (100 mg; 0,2 mmol) dissolved in 30 mL of dry acetone. Methyldiphenylphosphine, Ph₂PMe, (40 mg; 0,2 mmol) dissolved in 10 mL of acetone was then added dropwise and the mixture was stirred for 12h at 25°C. TICI was removed by filtration and the mixture purified through a CombiFlash chromatography. The product was precipitated with ether, in the form of a very fine orange powder, isolated yield: 60%.

NMR ³¹P {¹H} (121.49 MHz, CD₃CN, 25°C): δ = 27,3 (s, PPh₂Me), -144,6 (sept, ¹J_{P-F} = 705 Hz, PF₆⁻) ppm. NMR ¹H (300.10 MHz, CD₃CN, 25°C): δ = 9,31 (d, 1H), 8,87 (d, 1H), 8,42 (d, 1H), 8,38 (d, 1H), 8,16 (d, 1H), 8,02-7,98 (m, 2H), 7,97-7,92 (m, 2H), 7,70 (d, 1H), 7,66 (t, 1H), 7,39-7,33 (m, 7H), 7,29 (t, 1H), 7,24 (t, 2H), 7,20 (t, 2H), 7,14 (t, 2H), 7,00 (t, 1H), 1,52 (d, ²J_{P-H} = 8,2 Hz, 3H, PC<u>H₃</u>).

Note that this complex was previously prepared by Meyer and collaborators *via* another synthetical procedure (see: B. P. Sullivan, D. J. Salmon, T. J. Meyer, *Inorg. Chem.*, 1978, **17**, 3334).

Synthesis of [RuPMe]⁺-RuNPs.

As a general procedure, [Ru(cod)(cot)] (30.0 mg; 0.095 mmol) and $[RuPMe]^+$ (7.5 mg; 0.0095 mmol) were introduced in a Fisher-Porter reactor under Ar atmosphere, and dissolved in 30 mL of THF yielding an intense orange solution. The reactor was pressurized with 3 bar of hydrogen (H₂) at room temperature (r.t.) and under stirring. The initial orange solution turned black into a few minutes. Vigorous magnetic stirring and H₂ pressure were maintained for 24h at r.t. Then, excess H₂ was evacuated by pumping under vacuum. Evaporation of the solvent under vacuum induced the formation of a black precipitate. This solid was washed three times with THF (3x15mL), dried under vacuum and then re-dissolved in acetonitrile which led to an homogeneous colloidal dispersion. This colloidal dispersion was then transferred into a vial and dried under vacuum, leading to a dark black fine powder.

Control experiment on the fate of $[RuPMe]^{\dagger}[PF_6]$ complex under hydrogen atmosphere in the experimental reaction conditions used for the synthesis of the nanohybrid $[RuPMe]^{\dagger}$ -RuNPs

Complex [RuPMe]⁺PF₆⁻ (5 mg, mmol) was introduced into a Fischer-Porter reactor and dissolved in freshly dry and degassed THF (20 mL) under Ar atmosphere, leading to an orange solution. The reactor was then pressurized with 3 bar H2 at room temperature (r.t.) and under vigorous stirring. Magnetic stirring and H₂ pressure were maintained for 24h at r.t. after which no color change in the solution was observed. Evacuation of H₂ and removal of the volatiles by pumping under vacuum gave rise to an orange solid that was finally dissolved in CD₃CN for ¹H and ³¹P NMR analysis. The spectra recorded on the orange solid recovered after the control test were identical to those of the introduced [RuPMe]⁺PF₆⁻ complex indicating that complex [RuPMe]⁺PF₆⁻ kept its initial structure under the experimental reaction conditions used for the preparation of the nanohybrid [RuPMe]⁺-RuNPs.

Reaction of [RuPMe]⁺-RuNPs with ¹³CO

[RuPMe]⁺-RuNPs hybrid nanomaterial dispersed into SiO₂ was exposed to 1 atm of ¹³CO for 24h in a Fischer-Porter bottle. The excess of CO was then evacuated under vacuum and the hybrid sample introduced in an NMR rotor to be analyzed by ¹³C MAS solid-state NMR.

1.3. Characterization techniques.

Transmission Electron Microscopy (TEM) and High resolution TEM (HR-TEM). Samples for transmission electron microscopy (TEM) and high-resolution HR-TEM analyses were prepared by slow evaporation of a drop of an acetonitrile solution of purified [RuPMe]⁺-RuNPs deposited onto a holey carbon-covered copper grid. TEM analysis were performed on a MET JEOL JEM 1400 microscope operating at 120 kV with a resolution point of 0.45 nm. For HR-TEM, a JEOL JEM-ARM 200F microscope working at 200 kV with a resolution point of 0.19 nm was used. TEM allowed to evaluate the particle morphology, size and size distribution. Enlarged micrographs were used for treatment with ImageJ software to obtain a statistical size distribution (ca. 400 nanoparticles were manually measured) and the nanoparticle mean diameter. FFT treatments of HR-TEM images were carried out with Digital Micrograph Version 1.80.70 to determine the crystalline structure and lattice parameters of the metal nanoparticle.

Wide-angle X-ray scattering (WAXS). Measurements were performed at CEMES-CNRS in Toulouse. Samples were sealed in 1.0 mm diameter Lindemann glass capillaries. The samples were irradiated with graphite monochromatized molybdenum K α (0.071069 nm) radiation and the X-ray scattering intensity measurements were performed using a dedicated two-axis diffractometer. Radial distribution functions (RDF) were obtained after Fourier transformation of the corrected and reduced data.

Nuclear magnetic resonance (NMR) spectroscopy. Preparation of the samples for solution NMR studies was carried out under argon in a glove box using CD_3CN as a solvent. Liquid proton (¹H) and phosphorous (³¹P) NMR were performed on a Bruker Avance NEO 600 spectrometer at 296 K. DOSY measurements were acquired with a diffusion delay (Δ) of 130.0 ms and a gradient pulse length (δ) of 2.0 ms. The diffusion dimension was processed with bi-exponential analysis involving least-squares fitting or by the Laplace inversion routine CONTIN (Topspin software). The hydrodynamic diameter were calculated with the Stockes-Einstein Gierer-Wirtz estimation method (ref).

Solid-state NMR analysis was accomplished on a Bruker Avance III HD 400 wide-bore spectrometer. Due to electric arcing with the sample alone, the powder of [RuPMe]⁺-RuNPs was dispersed in mesoporous silica (60 Å). The silica matrix was impregnated with an acetonitrile solution of the sample, and solvent was evaporated under vacuum. Filling of the rotors (zirconia; diameter 3.2 mm) with the samples was performed in a glove box. Rotors were spun at 16 kHz at 298 K. ¹⁹F and ³¹P MAS NMR experiments were performed with recycle delays of 5 s and 2 s, respectively. ³¹P MAS NMR data were recorded with Hahn-echo and CPMG pulse sequences. ¹³C CPMAS spectra were acquired with a recycle delay of 2 s and a contact time of 3 ms.

Quantification of Hydrides

The quantification of hydrides present at the surface of [RuPMe]⁺-RuNPs nanomaterial was performed following a previously described procedure (<u>see</u> : J. García-Antón, M. Rosa Axet, S. Jansat, K. Philippot, B. Chaudret, T. Pery, G. Buntkowsky, H.-H. Limbach, Angew. Chem. Int. Ed., 2008, 47, 2074-2078; R. Gónzalez-Gómez, L. Cusinato, C. Bijani, Y. Coppel, P. Lecante, C. Amiens, I. del Rosal, K. Philippot, R. Poteau, Nanoscale, 2019, 19, 9392-9409.).

5 equivalents of 2-norbornene were added to a freshly prepared and degassed colloidal suspension of [RuPMe]⁺-RuNPs. The reaction mixture was maintained at r.t. under vigorous stirring for 72 h. Aliquots were taken for GC analysis (with calibration curve for norbornane) in order to estimate the conversion of norbornene into norbornane. The quantification of the alkane formed was estimated by considering the necessary amount of hydrogen to hydrogenate the alkene as determined by GC analysis (see below).

GC analyses were performed with a GCMS-QP2010 Ultra instrument equiped with a flame ionization detector and a Zebron ZB-5MSplus column (30m L x 0,25mm ID x 0,25µm df) 5% polysilarylene – 95% polydimethylsiloxane. Nitrogen UHP was used as carrier gas. Each analysis was performed using a temperature set from 30 to 250 °C (15° C.min⁻¹).

The H_{reac}/Ru_{surf} ratio was calculated considering the nanoparticle mean size measured by TEM, d_m , and the equations below.

Equation (1) was used to estimate the total number of atoms per nanoparticle, N_T

(1)
$$N_T = \left(\frac{d_m}{2r_{Ru}b}\right)^3$$

Where d_m is the nanoparticle diameter (measured by TEM), r_{Ru} is the atomic radii of a Ru atom and *b* is the crystalline closed-packed parameter (b=1,105)

Equations (2) and (3) were used to estimate the number of shells per nanoparticle, n, and the number of surface atoms, N_{surf} , respectively

(2)
$$N_T = \frac{1}{3} (10n^3 - 15n^2 + 11n - 3)$$

(3)
$$N_{surf} = 10n^2 - 20n + 12$$

The amount of H atoms involved in the reduction of norbornene, n_H , was calculated by equation (4), considering the quantity of norbornane produced as determined by GC.

(4)
$$n_H = 2 \cdot n_{norbornane}$$

Finally, the ratio H_{reac}/Ru_{surf} is obtained by equation (5)

(5)
$$H_{reac}/Ru_{surf} = \left(\frac{n_H}{n_{Ru}}\right) \left(\frac{N_{surf}}{N_T}\right)$$

where n_{Ru} are the mol of ruthenium introduced for the reaction.

X-ray photoelectron spectroscopy (XPS). XPS measurements were performed at CIRIMAT-ENSIACET, Toulouse. The photoelectron emission spectra were recorded using a monochromatised AI Kalpha (hv = 1486.6 eV) source on a ThermoScientific K-Alpha system. The X-ray Spot size was 400 μ m. The Pass energy was fixed at 30 eV with a step of 0.1 eV for core levels and 160 eV for surveys (step 1eV). The spectrometer energy calibration was done using the Ag3d_{5/2} (368.2 ± 0.1 eV) photoelectron lines. XPS spectra were recorded in direct mode N (Ec) and the background signal was removed using the Shirley method. XPS High Resolutions spectra were recorded in order to extract the chemical environments of the studied species.

2. Figures



Figure S1. TEM pictures of [RuPMe]⁺-RuNPs hybrid samples synthesized with a) 0.2, b) 0.1 and c) 0.01 equivalent of [RuPMe]⁺, after purification and redispersion in acetonitrile.



Figure S2. TEM pictures obtained from colloidal suspension of [RuPMe]⁺-RuNPs hybrid in THF.



Figure S3. (a) HRTEM image from colloidal suspension of [RuPMe]⁺-RuNPs in acetonitrile, the scale bar corresponds to 10 nm; (b) Fast Fourier Transformation (FFT) of HRTEM image (a) for the selected particle (red square).



Figure S4. (a) WAXS diagram of [RuPMe]⁺-RuNPs in comparison with diffraction pattern of bulk hcp Ru; (b) RDF of [RuPMe]⁺-RuNPs : experimental function (middle, black) with simulation from dual size model (middle, red), simulations from small model (top) and larger model (bottom).

Table S1. XPS data of free [RuPI	Me] ⁺ complex and	[RuPMe] ⁺ -RuNPs hybrid.
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Elements	[RuPMe] ⁺ complex	[RuPMe] [⁺] -RuNPs hybrid
Ru	B :Ru3d _{5/2} at 280.7eV (Ru-N)	A :Ru3d _{5/2} at 279.8eV (Ru metal)
	B'' :Ru sat 282.6eV (Ru-N)	A' : Ru3d _{3/2} at 284.0 (Ru metal)
	B' :Ru3d _{3/2} at 284.8eV (Ru-N)	B :Ru3d _{5/2} at 280.7 eV (Ru-N)
		B'' : Ru sat 282.6 eV (Ru-N)
		B' :Ru3d _{3/2} at 284.8 eV (Ru-N)
		C :Ru3d _{5/2} at 281.4eV (Ru-Cl)
		C' Ru3d _{3/2} at 285.5eV (Ru-Cl)
		C" Ru sat 286.7eV (Ru-Cl)
Р	E :P2p _{3/2} at 130.9eV (P-cycles)	E :P2p _{3/2} at 130.9eV (P-cycles)
	E' :P2p _{1/2} at 131.7 eV (P-cycles)	E' :P2p _{1/2} at 131.7 eV (P-cycles)
	F :P2p _{3/2} at 132.5 eV (P-CH3, PO possibly)	F :P2p _{3/2} at 132.5 eV (P-CH3, PO possibly)
	F' :P2p _{1/2} at 133.3 eV (P-CH3, PO possibly)	F' :P2p _{1/2} at 133.3 eV (P-CH3, PO possibly)
	G : P2p _{3/2} at 135.8 eV (P-F)	G :P2p _{3/2} at 135.8 eV (P-F)
	G' : P2p _{1/2} at 136.7 eV (P-F)	G' :P2p _{1/2} at 136.7 eV (P-F)
	H :P2p _{3/2} at 137.6 eV (Phosphorus salt)	
	H' :P2p _{1/2} at 138.4 eV (Phosphorus salt)	
N	J :N1s at 399.9eV (C-N-Ru)	I :N1s at 398.0eV (pyridinic)
		J : N1s at 399.9eV (C-N-Ru)







Figures S5. XPS spectra recorded for [RuPMe]⁺ complex and [RuPMe]⁺-RuNPs hybrid in the regions Ru3d, P2p, N1s, F1s and Cl2p.



Figure S6 ¹H NMR of [RuPMe]⁺-RuNPs hybrid in CD₃CN.



Figure S7 Single-exponential least-squares fitting analysis (left) and bi-exponential analysis least-square fitting (right) for RuPMe]⁺-RuNPs hybrid in CD₃CN. Clearly, the bi-exponential analysis is necessary to match the experimental data.



Figure S8 (top) ¹H NMR of free [RuPMe]⁺ and (bottom) ¹H diffusion-filtered NMR of [RuPMe]⁺-RuNPs hybrid in CD_3CN .



Figure S9 ³¹P NMR of (top) free [RuPMe]⁺ and (bottom) [RuPMe]⁺-RuNPs hybrid in CD₃CN.



Figure S10 ³¹P CPMG MAS NMR in SiO₂ of [RuPMe]⁺-RuNPs (blue) with signal deconvolution (black/red).



Figure S11 ¹³C MAS NMR in SiO₂ of (a) free $[RuPMe]^+$ and (b) $[RuPMe]^+$ -RuNPs hybrid.



(ppm) **Figure S12.** ¹⁹F solid-state NMR of (a) KPF₆, (b) $[RuPMe]^+$, (c) $[RuPMe]^+$ in SiO₂ and (d) $[RuPMe]^+$ -RuNPs in SiO₂.



Figure S13 ¹³C MAS NMR of [RuPMe]⁺-RuNPs hybrid after exposure under ¹³CO (1 atm; 24h; r.t.)

3. Details on Theoretical Calculations and corresponding figures

Computational details

Periodic DFT calculations of metal clusters.

Software: Vienna ab initio simulation package, VASP^[1,2]; spin polarized DFT; exchange-correlation potential approximated by the generalized gradient approach proposed by Perdew, Burke, and Ernzerhof (PBE)^[3]; projector augmented waves (PAW) full-potential reconstruction^[4,5]; PAW data sets for metal atoms treating the (n-1)p, (n-1)d and ns states (14 valence electrons for Ru); kinetic energy cutoff: 525 eV; Γ -centered calculations^[6]; Gaussian smearing of 0.02 eV width; geometry optimization threshold: residual forces on any direction less than 0.02 eV/Å; supercell size: 40×39,5×39 Å for Ru55 clusters and 28×28.25×25.5 Å for Ru13 nanoclusters (set to ensure a vacuum space of ca. 16 Å between periodic images of metal clusters). The reaction barriers were estimated by the climbing image nudge elastic band (CINEB) method^[7,8,9] with a spring force between images of 5 eV and a force tolerance of 0.02 eV/Å. The harmonic vibrational modes were systematically calculated for in order to distinguish minima and saddle points by using the dynamical matrix code implemented in VASP as well as the VASPTST tools also developed in Henkelman's group.

NMR Calculation

Software: Gaussian09; ^[10] geometries fully optimized without any geometry constraints; B3PW91 hybrid functional ^[11,12,13,14,15,16]; Chemical shielding tensors: Gauge Including Atomic Orbital (GIAO) method. ^[17,18,19,20,21]; Relativistic effective core potentials developed by the Stuttgart group and their associated basis sets have been used for Ru ^[22] - augmented with an f polarization function (ζ_f : 1.235); P, F, C and O: 6-31G(d,p) basis set. ^[23,24] The optimized structures were used for ³¹P and ¹⁹F NMR calculations. Typically, in order to compare our calculations with experimental values, ³¹P and ¹⁹F chemical shieldings have been converted to chemical shifts using the usual equation $\delta_{iso} = \sigma_{iso,ref} - \sigma_{iso,sample}$, where $\sigma_{iso,ref}$ is the isotropic chemical shielding of ³¹P in 85% Phosphoric Acid or of ¹⁹F in trichlorofluoromethane. In our case, $\sigma_{iso,ref}$ (³¹P) = 330,24 ppm and $\sigma_{iso,ref}$ (¹⁹F) = 186,87 ppm.



Figure S14. Stable coordination modes of the [RuPMe]⁺ complex at the RuNP surface. Adsorption energies, in red, are given in kcal/mol.

PF₆ interaction with RuNP surface



Fig S15. Calculated ³¹P and ¹⁹F NMR displacements for PF₆ coordinated on a [Ru₆] cluster model.

Following a computational strategy successfully used for computing ¹H, ¹³C and ¹⁵N chemical shits, a [Ru6] carbonyl cluster was first used as a model for Ru Nps.^[25,26,27] The ³¹P and ¹⁹F chemical shifts were calculated by DFT tudies and compared with the observed ones. When PF₆⁻ bridges two adjacent Ru atoms, the estimated ¹⁹F chemical shifts are between -104 ppm and -188 ppm for the F atom directly coordinated to the Ru cluster surface and between -55 ppm and -79 ppm for the other ones. In the same way, the coordination of the PF₆⁻ anion is expected to unshield the phosphorus chemical shift by around 25 ppm with respect to the free PF₆⁻ anion. In summary, according to the theoretical calculations when the PF₆⁻ anion is coordinated at the RuNP surface the Fluor atoms interacting with the surface are more shielded (by around 50 ppm) while a deshielding is observed for Phosphorus (by around 17 ppm). Thus, in view of these results, DFT calculations corroborate that the PF₆⁻ anion does not interact with the RuNP surface.



Figure S16. (a) Comparison of the X-Ray and PBE-DFT geometries; (b) Characteristic bond lengths in the most stable coordination mode of the [RuPMe]⁺ complex (see Fig. 3 of the paper, and Fig. S14b)





Figure S17. Two possible coordination modes on a Ru13H17 scale model (see also Ref. 28). Energy of the [RuPMe]⁺ complex after Ru-Cl cleavage with respect to the undissociated complex. Energy differences, in red, are given in kcal/mol.

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