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

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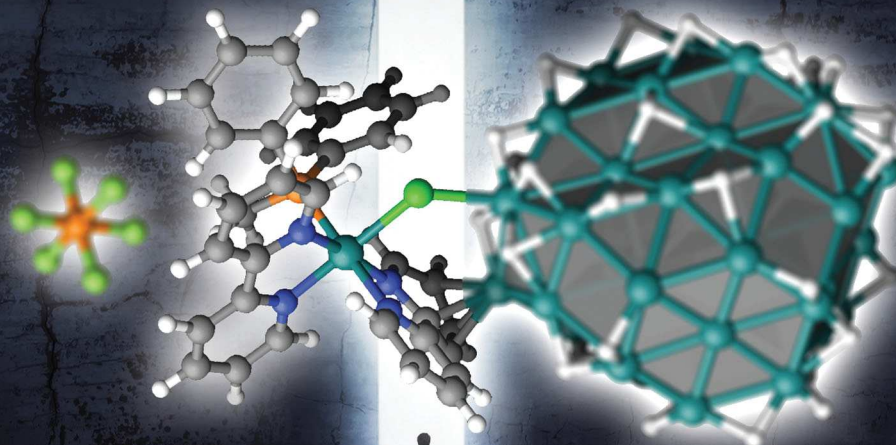
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**NEW AVENUES TOWARDS THE PREPARATION OF  
HYBRID NANOMATERIALS**

Showcasing research from Dr Sutra, Dr Philippot and Dr Igau's laboratory, Laboratoire de Chimie de Coordination, Toulouse, France. This illustration is designed by Arnaud Laplace from CLEARTRADE ([www.cleartrade.fr](http://www.cleartrade.fr)).

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

A hybrid material made of mononuclear organophosphorus polypyridyl ruthenium complexes covalently bonded to ruthenium nanoparticles has been synthesized *via* a one-pot organometallic procedure and finely characterized. These results open new avenues to access unique hybrid transition metal nanomaterials.

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

DOI: 10.1039/d0cc00442a

Elena Martín Morales,<sup>ab</sup> Yannick Coppel,<sup>ab</sup> Pierre Lecante,<sup>c</sup> Iker del Rosal,<sup>d</sup> Romuald Poteau,<sup>id</sup> Jérôme Esvan,<sup>e</sup> Pierre Sutra,<sup>\*ab</sup> Karine Philippot<sup>id</sup> <sup>\*ab</sup> and Alain Igau<sup>id</sup> <sup>\*ab</sup>

**A hybrid material made of mononuclear organophosphorus polypyridyl ruthenium complexes covalently bonded to ruthenium nanoparticles has been synthesized via a one-pot organometallic procedure and finely characterized. These results open new avenues to access unique hybrid transition metal nanomaterials.**

Because of their remarkable activities and selectivities, transition metal complexes (TMCs) are actively investigated towards catalytic,<sup>1</sup> optoelectronic,<sup>2</sup> and medicinal applications.<sup>3</sup> It is well-established that the interplay between the ligands and the metal center strongly influences the TMC performance. Appropriate TMCs can be used as precursors for the synthesis of metal nanoparticles (MNPs) in the presence of stabilizing agents (polymers, surfactants, ligands, *etc.*), usually under mild conditions.<sup>4,5</sup> This synthetic pathway is one of the most efficient methods to provide well-controlled MNPs with reproducible physicochemical properties which make them attractive materials for various applications such as those mentioned above for TMCs.<sup>6</sup> As observed for ligands coordinated on the metal center of TMCs, the performance of the MNPs is highly dependent on the interplay between the stabilizer and the metal surface.<sup>7</sup>

In the late 1990s,<sup>8</sup> TMCs have started to be associated with MNPs using organic spacers containing pendant ligands mostly by a post functionalization procedure involving ligand exchange reactions at the surface of the NPs.<sup>9,10</sup> We report here the direct

synthesis of small ruthenium NPs stabilized by organophosphorus ruthenium polypyridine complexes.

The preparation of ruthenium nanoparticles (RuNPs) from the olefinic precursor [Ru(COD)(COT)] in the presence of various stabilizers and under mild conditions is a well-mastered synthesis method in our laboratory, being part of the organometallic approach.<sup>11</sup> This approach provides well-defined RuNPs that can serve as models for fundamental studies. In addition, our long-standing interest in the properties of organophosphorus ruthenium(II) polypyridine complexes,<sup>12</sup> as well as their remarkable chemical robustness, prompted us to explore the capability of these TMCs to coordinate onto the surface of RuNPs and stabilize them. For this purpose, we selected the mononuclear cationic organophosphorus polypyridyl ruthenium complex [(bpy)<sub>2</sub>Ru(Ph<sub>2</sub>PMe)Cl]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (labelled as [RuPMe]<sup>+</sup>). Besides the phosphorus atoms and the methyl fragment which are powerful probes in <sup>31</sup>P and <sup>1</sup>H NMR, respectively, the chlorine atom in [RuPMe]<sup>+</sup> is anticipated to act as an atomic linker<sup>13</sup> between the organophosphorus polypyridyl ruthenium complex and the halophilic metallic surface of the RuNPs.

We thus describe hereafter the synthesis of a novel hybrid nanomaterial, namely [RuPMe]<sup>+</sup>-RuNP, and its full characterization by a combination of experimental analysis techniques and theoretical calculations. This work reports an effective way to potentially access a new family of hybrid nanomaterials.

In a Fischer-Porter reactor, the usual conditions of the organometallic approach (3 bar H<sub>2</sub>, vigorous stirring, r.t., 24 h) were applied in order to decompose the [Ru(COD)(COT)] precursor in the presence of [RuPMe]<sup>+</sup> as a stabilizer. A series of reactions have been performed at a different [RuPMe]<sup>+</sup>/[Ru(COD)(COT)] ratio (0.2, 0.1, and 0.01 eq. of [RuPMe]<sup>+</sup>). The initial orange solution turned rapidly black after pressurization of the reactor with hydrogen. Black precipitates were obtained in all cases which could be washed with THF and re-dispersed in acetonitrile for TEM (transmission electron microscopy) study (Fig. S1, ESI†). No major difference in the size, dispersion and homogeneity of the RuNPs was observed between 0.2 and 0.1 eq. of [RuPMe]<sup>+</sup>. For 0.01 eq., big and non-dispersible aggregates were mostly

<sup>a</sup> Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, F-31077, Toulouse Cedex 04, France

<sup>b</sup> Université de Toulouse, UPS, INPT, LCC, F-31077 Toulouse Cedex 04, France.  
E-mail: pierre.sutra@lcc-toulouse.fr, Karine.Philippot@lcc-toulouse.fr, alain.igau@lcc-toulouse.fr

<sup>c</sup> CEMES-CNRS, 29 rue Jeanne Marvig BP4347, 31053 Toulouse Cedex, France

<sup>d</sup> LPCNO (IRSAMC), Université de Toulouse, INSA, UPS, CNRS (UMR 5215), Institut National des Sciences Appliquées, 135 avenue de Rangueil, F-31077 Toulouse, France

<sup>e</sup> CIRIMAT, Université de Toulouse, CNRS-INPT-UPS, 4 Allée Emile Monso, BP 44362, 31030 Toulouse, France

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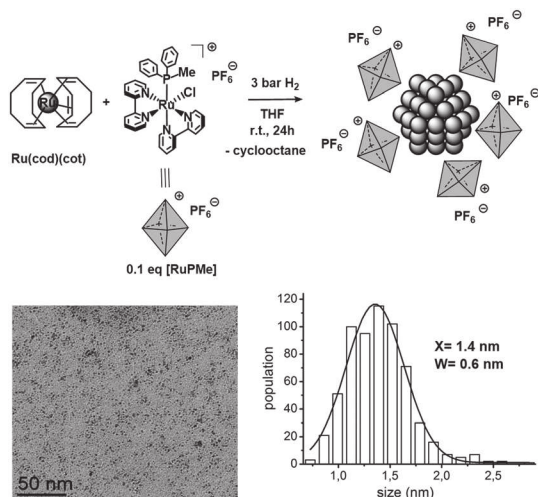


Fig. 1 Synthesis and TEM image with a size histogram of the  $[\text{RuPMe}]^+$ -RuNP hybrid (0.1 eq. of  $[\text{RuPMe}]^+$ ), cod =  $\eta^4$ -1,5-cyclooctadiene; cot =  $\eta^6$ -1,3,5-cyclooctatriene.

observed together with a few small and individual nanoparticles. This series of syntheses evidenced the efficient stabilizing effect of the  $[\text{RuPMe}]^+$  complex at a quite low quantity of complex. In order to minimize the excess Ru-complex, we then focused on the hybrid nanomaterial  $[\text{RuPMe}]^+$ -RuNP prepared with 0.1 eq. of  $[\text{RuPMe}]^+$ .

This material contains small and well-dispersed individual NPs with a quite symmetrical but large size distribution centered at *ca.* 1.4 nm  $\pm$  0.6 (Fig. 1). This image is different from that of the crude colloidal suspension in THF where regular spherical aggregates of *ca.* 350 nm composed of individual NPs were visible (Fig. S2, ESI<sup>†</sup>). This difference of dispersion of the NPs can be explained by the different solubility of the nanomaterial in THF and in acetonitrile, the latter being more polar. This experimental observation may reflect the transfer of the ionic nature of the molecular complex  $[\text{RuPMe}]^+$  onto the nanomaterial.

A HRTEM (high-resolution transmission electron microscopy) image recorded for  $[\text{RuPMe}]^+$ -RuNP dispersed in  $\text{CH}_3\text{CN}$  evidenced a heterogeneous population of particles. While the small NPs (main population) are amorphous, some bigger ones (*ca.* 2.6 nm) display crystalline planes related to a hexagonal close-packed (hcp) structure as determined by Fast Fourier Transform (FFT) (Fig. S3, ESI<sup>†</sup>). These results were mostly confirmed by Wide-Angle X-ray Scattering (WAXS) on the powder of  $[\text{RuPMe}]^+$ -RuNP (Fig. S4, ESI<sup>†</sup>). The coherence length could be estimated to be *ca.* 2.5 nm which is in accordance with the estimated size of big and crystalline RuNPs observed by HRTEM. However a better fitting was obtained using a dual size model computed from the hcp network: small NPs (1.3 nm in size) required for the fast decrease of the RDF at short distances and larger ones (2.5 nm in size) generating the longer distances.

X-Ray photoelectron spectroscopy (XPS) analysis of the  $[\text{RuPMe}]^+$ -RuNP hybrid was also investigated in comparison to that of the free  $[\text{RuPMe}]^+$  complex (Fig. S5 and Table S1, ESI<sup>†</sup>). In accord with  $[\text{RuPMe}]^+$  data, the spectrum of the hybrid presents signals in the Ru3d region that can be assigned to the coordinated  $[\text{RuPMe}]^+$  (280.7, 282.6 and 284.8 eV for Ru3d<sub>5/2</sub>,

Ru3d<sub>3/2</sub> and Ru3d satellites, respectively) in addition to the peaks for metallic Ru from the RuNPs (279.8 and 284 eV for Ru3d<sub>5/2</sub> and Ru3d<sub>3/2</sub>, respectively).<sup>14</sup> The P2p region shows signals matching with the  $\text{PF}_6^-$  counteranion (135.8 and 136.7 eV) and  $\text{Ph}_2\text{PMe}$  ligand of the  $[\text{RuPMe}]^+$  complex (130.9, 131.7, 132.5 and 133.3 eV). In the N1s region, the peak at 399.9 eV corresponds to the C-N-Ru bonds of the bipyridine ligands on the  $[\text{RuPMe}]^+$  complex while that at 398.0 eV indicates another chemical environment for these ligands, which maybe due to the proximity with the NP metal surface.

Liquid and solid state NMR spectroscopy analysis on the hybrid material provided deep information on the nature of the interaction of the  $[\text{RuPMe}]^+$  complex with the RuNPs.

In comparison to the data of the complex alone, the <sup>1</sup>H-NMR spectrum of purified  $[\text{RuPMe}]^+$ -RuNP in  $\text{CD}_3\text{CN}$  (Fig. S6, ESI<sup>†</sup>) revealed a characteristic pattern of signals attributed to the  $[\text{RuPMe}]^+$  complex. The signal broadening observed for the aliphatic P-Me protons (*ca.* 1.75 ppm) and the aryl phenyl and bipyridine protons (between 6.5 and 9.5 ppm) is the signature of the close interaction of the  $[\text{RuPMe}]^+$  complex with the metal surface of the RuNPs which limits their motion. Residual sharp peaks matching those of  $[\text{RuPMe}]^+$  are also identified. These peaks are too sharp to belong to  $[\text{RuPMe}]^+$  entities directly coordinated to the RuNP surface (inner layer) but significantly broader than those of the  $[\text{RuPMe}]^+$  complex alone in solution. They can be attributed to  $[\text{RuPMe}]^+$  species present in the outer layer of the  $[\text{RuPMe}]^+$ -RuNP hybrid material which are in strong electrostatic interaction with those of the inner layer that may explain why they were not removed during the purification step. This is confirmed by the DOSY NMR experiment (Fig. 2, right). The diffusion curve can be fitted with two diffusion coefficients (Fig. S7, ESI<sup>†</sup>), namely  $D_{\text{hybrid}} = 4.0(\pm 0.2) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  and  $D_{\text{exch}} = 10.0(\pm 0.3) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , with a population ratio of 60/40( $\pm 5$ ). 2D DOSY processing with the Contin method showed that the particles have probably a more polydisperse size distribution. The diffusion coefficient measured for the free mononuclear complex  $[\text{RuPMe}]^+$  has a value of  $D_{[\text{RuPMe}]^+} = 1.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . The lowest value,  $D_{\text{hybrid}}$ , corresponds to the hybrid material in which the  $[\text{RuPMe}]^+$  complex is coordinated to the surface of RuNPs. The highest value,  $D_{\text{exch}}$ , can be reasonably assigned to the ionic  $[\text{RuPMe}]^+$  species in dynamic exchange *via* electrostatic interactions

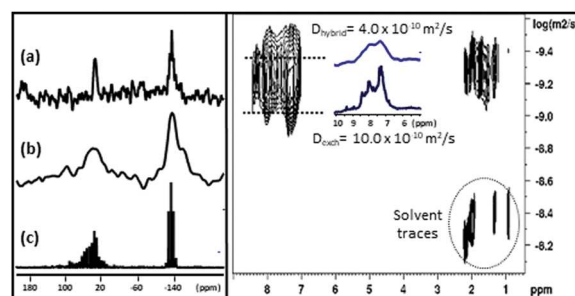


Fig. 2 (left) <sup>31</sup>P MAS NMR in  $\text{SiO}_2$  of (a) free  $[\text{RuPMe}]^+$  and of the  $[\text{RuPMe}]^+$ -RuNP hybrid with the (b) Hahn-echo and (c) <sup>31</sup>P cpmg method. (right) 2D DOSY of  $[\text{RuPMe}]^+$ -RuNP in  $\text{CD}_3\text{CN}$  with  $D_{\text{hybrid}}$  and  $D_{\text{exch}}$  entities.

between free and outer-sphere complexes in solution. A hydrodynamic diameter of *ca.* 3.2 nm was determined using the Stokes–Einstein–Gierer–Wirtz estimation method<sup>15</sup> for hybrid material [RuPMe]<sup>+</sup>–RuNP diffusing at  $D_{\text{hybrid}}$ . Under the same conditions, the diffusion coefficient of the [RuPMe]<sup>+</sup> complex led to a hydrodynamic diameter of *ca.* 0.9 nm. Given that a mean size of *ca.* 1.4 nm was calculated for the particles from TEM analysis (corresponding to the metal core) one can estimate that [RuPMe]<sup>+</sup>–RuNP made of a Ru core surrounded by a layer of [RuPMe]<sup>+</sup> complexes would be higher than 3.0 nm. Thus the value obtained from  $D_{\text{hybrid}}$  is in very good accordance with such a hypothesis.

The <sup>1</sup>H-NMR signal of the hybrid material can be more clearly observed with a diffusion filter (Fig. S8, ESI<sup>†</sup>), where only the broad signals, characteristic of [RuPMe]<sup>+</sup> in close contact with the RuNPs, are kept (the signals of the fast diffusing [RuPMe]<sup>+</sup> of the outer layer being eliminated from the spectrum).

In the liquid <sup>31</sup>P-NMR spectrum, the sharp and well resolved septuplet centered at –144.6 ppm corresponds to the PF<sub>6</sub><sup>–</sup> anion (Fig. S9, ESI<sup>†</sup>) and indicates that PF<sub>6</sub><sup>–</sup> is totally solvated by acetonitrile and located away from the influence of the RuNPs, thus, preserving its molecular dynamics. Also a sharp signal of low intensity is visible at 27.3 ppm which can be attributed to [RuPMe]<sup>+</sup> complexes at the periphery of the [RuPMe]<sup>+</sup>–RuNP hybrid material as also identified by <sup>1</sup>H-NMR. No signal attributable to the phosphine Ph<sub>2</sub>PMe ligand of the [RuPMe]<sup>+</sup> complex in direct interaction with the NP surface is observed. But this is not surprising since it is well established that organophosphorus fragments that are close to a metal surface are not expected to be observed by liquid <sup>31</sup>P NMR experiments.<sup>16</sup>

Magic angle spinning (MAS) solid state NMR spectra were recorded for the hybrid material [RuPMe]<sup>+</sup>–RuNP after its dispersion in silica in order to avoid electric arcing with the NMR coil (see the ESI<sup>†</sup> for preparation details). The results were compared with those obtained for the free [RuPMe]<sup>+</sup> complex under the same conditions. Like for solution NMR spectra, the solid-state <sup>31</sup>P MAS NMR spectra of [RuPMe]<sup>+</sup>–RuNP present comparable features to that observed for the free [RuPMe]<sup>+</sup> complex but with broader signals due to local structural heterogeneity (Fig. 2, left). The Carr–Purcell–Meiboom–Gill (CPMG) sequence<sup>17</sup> allowed increasing the signal to noise ratio thus evidencing three main signals (Fig. S10, ESI<sup>†</sup>). An intense sharp signal is visible at –142.7 ppm that corresponds to PF<sub>6</sub><sup>–</sup>. Then, two overlapping signals at 25.7 and 33.3 ppm are identified. The sharp signal at 25.7 ppm can be attributed to [RuPMe]<sup>+</sup> species in the outer layer of the RuNPs, comparatively to solution NMR data. The broad one centered at 33.3 ppm is characteristic of a phosphorus atom affected by the heterogeneity of a metal surface as it was previously observed for phosphine-stabilized RuNPs.<sup>18</sup> It can thus be attributed to the Ph<sub>2</sub>PMe ligand of [RuPMe]<sup>+</sup> species directly interacting with the RuNPs, namely forming the inner layer of the stabilizer. The <sup>13</sup>C MAS solid-state NMR spectrum of the hybrid displays signals in the range of 110–180 ppm, and a signal at *ca.* 28 ppm, corresponding to aromatic and aliphatic carbons, respectively (Fig. S11, ESI<sup>†</sup>). If from these data we cannot totally exclude partial

hydrogenation of the phenyl group of the phosphine ligand, it clearly appears that the signature of the [RuPMe]<sup>+</sup> complex in the hybrid material [RuPMe]<sup>+</sup>–RuNP is preserved. The <sup>19</sup>F MAS solid state NMR spectrum of the hybrid evidenced the presence of only one signal at –75 ppm, in the same region as for the KPF<sub>6</sub> salt (Fig. S12, ESI<sup>†</sup>). This result confirms that the PF<sub>6</sub><sup>–</sup> anion does not interact with the surface of the RuNPs but is in electrostatic interaction with the [RuPMe]<sup>+</sup>–RuNP hybrid material.

All these NMR results enable us to propose that the cationic [RuPMe]<sup>+</sup> complex intervenes in the stabilization of the RuNPs at two different levels: a part (*ca.* 60%) is directly coordinated to the metal surface and forms a stabilizing inner layer and a second part (*ca.* 40%) surrounds the hybrids *via* electrostatic interactions. This double layer concept has already been reported in the literature for MNPs stabilized by charged species as quaternary ammonium<sup>19</sup> or ionic liquids.<sup>20</sup>

As already demonstrated in the group with ligand-stabilized RuNPs,<sup>6</sup> hydrides can be present at the metal surface of [RuPMe]<sup>+</sup>–RuNP due to synthesis conditions. The catalytic reduction of norbornene by a degassed colloidal suspension of freshly prepared [RuPMe]<sup>+</sup>–RuNP allowed us to identify hydrides at the surface of the particles with an estimated quantity of *ca.* 1.6H per Ru<sub>surf</sub> (see the ESI<sup>†</sup>). This value is close to the highest limit of the value range previously observed (0.2 to 1.5H<sup>–</sup> per Ru<sub>surf</sub>). This result indicates that the surface of [RuPMe]<sup>+</sup>-stabilized RuNPs remains accessible despite the presence of the stabilizer and can accommodate a high quantity of hydrides. To complete the characterization of the surface of the hybrid nanomaterial, a purified [RuPMe]<sup>+</sup>–RuNP sample was reacted with <sup>13</sup>CO (1 bar for 24 h). CO is known to coordinate at the surface of RuNPs in different coordination modes, mainly terminal and bridging ones, which provides characteristic signals in the <sup>13</sup>C MAS solid-state NMR spectrum.<sup>21</sup> Besides the signals corresponding to [RuPMe]<sup>+</sup> complexes, a signal is identified at *ca.* 190 ppm which can be attributed to CO coordinated in a terminal mode (Fig. S11, ESI<sup>†</sup>). These results confirm that the surface of [RuPMe]<sup>+</sup>-stabilized RuNPs accommodates CO molecules.

With the aim to get deeper information on the interaction modes of the [RuPMe]<sup>+</sup> complexes with the metallic surface in the [RuPMe]<sup>+</sup>–RuNP hybrid, density functional theory (DFT) calculations were performed on a 1 nm hydrogenated (0.8H per Ru<sub>surf</sub>) RuNP model (Ru<sub>55</sub>H<sub>35</sub>).<sup>22</sup> These studies revealed that the coordination of the [RuPMe]<sup>+</sup> complex at the RuNP surface occurs through the  $\sigma$ -donation of the chlorine lone pair atom with a binding energy (BE) of –33.8 kcal mol<sup>–1</sup> (Fig. S14a, ESI<sup>†</sup>). As it is commonly observed for some dimeric TMCs, in the hybrid, the chlorine atom acts as a bridging ligand between the [RuPMe]<sup>+</sup> complexes and the RuNP metal surface (Fig. 3). Moreover, the computational studies showed that the more stable hybrid conformer provides an additional aromatic  $\pi$ -type chelating interaction between one of the bipyridine ligands of the [RuPMe]<sup>+</sup> complex and one ruthenium surface atom of the RuNP (Fig. 3 and Fig. S14b, ESI<sup>†</sup>) (BE = –41.4 kcal mol<sup>–1</sup>). It is noteworthy that the interaction of the PF<sub>6</sub><sup>–</sup> anion with the metal surface is disfavored by *ca.* 7 kcal mol<sup>–1</sup> (Fig. S14, ESI<sup>†</sup>).

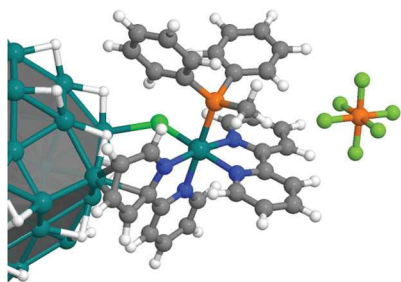


Fig. 3 Most stable coordination mode of the  $[\text{RuPMe}]^+$  complex at the RuNP surface.

In agreement with experimental and DFT NMR data (regarding DFT NMR, see Fig. S15, ESI<sup>†</sup> and the corresponding discussion), these results indicate that the  $\text{PF}_6^-$  anion lies in the outer sphere of the  $[\text{RuPMe}]^+$ -RuNP hybrid.

From a structural point of view (Fig. S16, ESI<sup>†</sup> for complementary details), coordination of  $[\text{RuPMe}]^+$  at the RuNP surface induces only slight geometrical modifications on the complex as indicated by the elongation of the Ru-Cl bond (by 0.05 Å) and for the C-N and C-C bonds of the bipyridine ligand interacting with the surface (by 0.07 and 0.04 Å, respectively).

Note that the cleavage of the Ru-Cl bond by the RuNP surface (Fig. S14d, ESI<sup>†</sup>) followed by the formation of a Ru-Ru bond and  $\mu$ -Cl capping one edge of the RuNP is slightly disfavored with a thermal endothermic value  $\Delta E$  of 1.1 kcal mol<sup>-1</sup>. However, this somewhat low energy difference could be questioned. This is why other energy clues have been calculated from a  $\text{Ru}_{13}\text{H}_{17}$  model cluster (see Fig. S17, ESI<sup>†</sup>).<sup>22</sup> It appears that in the two considered coordination modes (one very similar to the one depicted in Fig. 3 whilst the second one could occur on sharp apexes) the un-dissociated  $[\text{RuPMe}]^+$  complex is thermodynamically more stable than its dissociated counterpart by ca. 10 kcal mol<sup>-1</sup>. This supports that the adsorbed  $[\text{RuPMe}]^+$  keeps its structural integrity and identity.

In conclusion, we report here the synthesis of a unique hybrid material made of mononuclear organophosphorus polypyridyl ruthenium complexes acting as stabilizers of ruthenium nanoparticles under one pot conditions. Advanced NMR experiments evidenced the covalent coordination of the organophosphorus polypyridyl complex at the metal surface into an inner layer and the presence of other complex entities surrounding the hybrids thus forming an outer layer. Due to its cationic character, the  $[\text{RuPMe}]^+$  complex, in the outer layer, displays electrostatic interaction with its counterparts from the inner layer. Theoretical calculations evidenced that the coordination of the complex at the metal surface occurs *via* the chlorine atom of the complex, thus acting as a bridging ligand between the two entities of the hybrid nanomaterial. The stabilization of the hybrid is reinforced by an aromatic  $\pi$  interaction between one of the bpy ligands of the complex and the metal surface. Our results open new avenues towards the preparation of hybrid

nanomaterials with tunable properties towards a large domain of applications.

## Conflicts of interest

There are no conflicts to declare.

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