

Fine-Tuning HER Activity Through the Interplay Between Nanoparticle Size and Ligand Coordination Mode in Surface-Functionalized Nanocatalysts

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Cite This: *ACS Catal.* 2026, 16, 10337–10347



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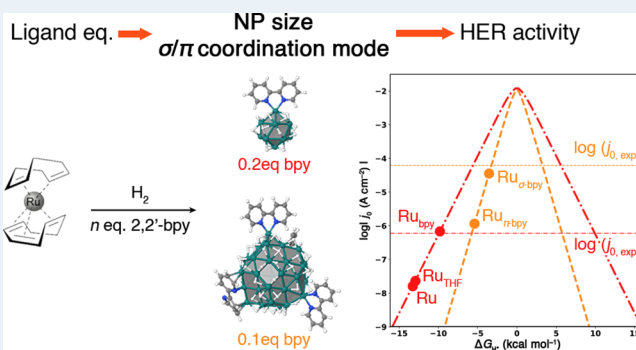
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ABSTRACT: Metallic nanoparticles (NPs) are state-of-the-art catalysts for the hydrogen evolution reaction (HER), and surface functionalization provides a powerful tool to tune both their physical properties and catalytic performance. This work explores the influence of stabilizing ligands on the HER performance of Ru NPs. We report Ru NPs functionalized with controlled amounts of 2,2'-bipyridine (bpy). The ligand loading has the usual influence on the NP size, as higher bpy concentrations produce smaller NPs. In contrast, the NP size affects the HER activity in a counterintuitive manner: the smallest NPs are the least active, whereas the largest ones achieve catalytic performance comparable to that of commercial Pt/C. Detailed compositional, spectroscopic, and electrochemical characterization, including analysis of bpy coordination via N 1s XPS, enabled the construction of *quasi*-realistic computational models. DFT calculations combined with the Yang and Saidi electrochemical model reveal that HER activity depends on both NP size and ligand coordination mode. Importantly, we provide direct evidence that σ - versus π -coordination of bpy controls the intrinsic HER catalytic activity of distinct Ru sites, as only the DFT-calculated exchange current density of σ -coordinated sites matches experimental trends. These results establish ligand coordination mode as a decisive descriptor in surface-functionalized nanocatalysts and introduce an additional design principle for developing highly efficient HER electrocatalysts.

KEYWORDS: hydrogen evolution reaction, ruthenium, nanoparticles, nanocatalysis, surface functionalisation



1. INTRODUCTION

The current climate situation is one of the main concerns of our society and a major challenge for the scientific community. The large consumption of fossil fuels—which are the undisputed source of energy as of today—and the carbon emissions associated with their combustion play a major role in this issue. Therefore, there is a pressing need for new energy sources that are clean, renewable, and carbon-free.¹

A promising solution is the production of H₂ from water powered by renewable energy sources.^{2,3} Nevertheless, the reactions entailed in water-splitting—especially the oxygen evolution reaction (OER), but also the hydrogen evolution reaction (HER)—present a certain degree of mechanistic complexity and, therefore, slow reaction kinetics. Thus, the use of suitable catalysts is indispensable to make the HER feasible for practical applications.⁴ In this regard, metallic nanoparticles (NPs) have increased their popularity in recent years as potential catalysts, given their unique nanoscale-derived properties.^{5–7}

Among the numerous methods reported for the synthesis of nanostructures,^{8,9} the organometallic approach is of particular interest. It entails the controlled decomposition of an organometallic precursor under mild conditions in the presence of a stabilizing ligand, both of which are generally rationally chosen. Typically, the organometallic precursor consists of a complex with olefinic ligands, and its decomposition is carried out by means of hydrogenation of their double bonds. The resulting alkanes no longer have coordinative ability and can be easily removed from the reaction medium.^{10,11} Unlike other methods that use inorganic salts or

Received: February 17, 2026

Revised: April 23, 2026

Accepted: April 24, 2026

Published: May 26, 2026



involve a multi-step process,^{12–15} the organometallic approach is a one-pot synthesis that yields NPs with a controlled surface free of contaminant by-products, containing only metal atoms and the desired ligand introduced as a stabilizer. This facilitates the study of the effects of said ligands on the NPs by enabling the development of more accurate models for their computational study and consequent rational improvement.

Regarding the HER, the metal–hydrogen (M–H) bond energy is a particularly relevant descriptor of the catalytic activity, given that the reaction mechanism involves the adsorption and desorption of hydrogen. According to the Sabatier principle, the M–H bond energy must be neither excessively strong nor overly weak. Theoretical calculations showed that the most optimal value for this process would be a M–H bond Gibbs free energy of 0 kcal mol^{−1}.¹⁶ In this regard, Pt-based materials are the benchmark catalysts for the HER since the energy of the Pt–H bond is the closest to the ideal value, slightly in excess of it.¹⁷ However, optimal M–H bond energies can also be achieved with other metals by surface functionalization with ligands.^{18,19} One good example can be found in Ru NPs. The Ru–H bond energy is slightly stronger than that of Pt, and hence, it is less active towards the HER. Nevertheless, we previously demonstrated how Ru NPs stabilized with 4-phenylpyridine (4PP) present an outstanding catalytic performance in the HER, outperforming commercial Ru-black and Pt/C in both basic and acidic media.²⁰ DFT calculations revealed that 4PP ligands shift the Ru–H bond energy of specific sites to the optimal value of 0 kcal mol^{−1}, not only improving the Ru–H bond energy of bare Ru NPs, but also surpassing that of Pt, thus proving the interest of looking for appropriate ligands to boost the performance of Ru nanocatalysts.²¹

To expand upon this previous work, and inspired by numerous examples of molecular Ru complexes for water splitting containing chelating pyridine ligands,^{22,23} we report four systems of Ru NPs stabilized with different equivalents of the 2,2′-bipyridine (bpy) ligand. The amount of bpy added for the synthesis influences the size of the resulting NPs, which also translates into different catalytic performances. Thorough characterization of these systems by analytical and spectroscopical techniques, including the elucidation of the coordination mode of the bpy ligand onto the NP surface, has led to the development of unprecedented *quasi*-realistic models for the computational study of these systems. With them, the ligand effect on the ΔG_{H^*} has been studied for different NP sizes, which unveils the factors ruling the observed HER performance in each system.

2. RESULTS AND DISCUSSION

Ru NPs were synthesised by an organometallic approach, as seen in Figure 1. A solution of the Ru precursor [Ru(cod)(cot)] (cod = 1,3-cyclooctadiene, cot = 1,3,5-cyclooctatriene) and the stabilizing ligand 2,2′-bipyridine in THF was hydrogenated under 3 bars of H₂ at room temperature. The resulting black dispersion was mixed with hexane to allow the sedimentation of the NPs, which were then isolated and dried under vacuum. Given that small Ru NPs are known to burn spontaneously under air exposure,²⁴ the as-synthesized NPs were stored in an Ar-filled vial and allowed to passivate by slow air diffusion for ca. four weeks. Following this approach, four systems were prepared using different molar equivalents (eq) of 2,2′-bipyridine, namely, 0.2, 0.1, 0.05, and 0.025

eq (Rubpy-0.2eq, Rubpy-0.1eq, Rubpy-0.05eq, and Rubpy-0.025eq, respectively). The samples were analyzed by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and small spherical NPs were found in all systems (Figure 1B–E). The four systems presented mean sizes of 0.8 ± 0.1 nm (Rubpy-0.2eq), 1.3 ± 0.2 nm (Rubpy-0.1eq), 1.8 ± 0.2 nm (Rubpy-0.05eq), and 2.4 ± 0.4 nm (Rubpy-0.025eq). It can also be observed how the NPs with fewer ligands (Figure 1E) are more prone to aggregate than the NPs with a larger amount of the stabilizer (Figure 1B), owing to the lesser degree of steric stabilization stemming from lower ligand concentration on their surface. This shows that the larger the amount of the bpy ligand added during the synthesis, the smaller and better dispersed the resulting NPs are. According to the literature, this might suggest a strong coordination of the bpy ligand to the Ru surface.²⁵

Inductively coupled plasma optical emission spectroscopy (ICP-OES) and elemental analysis were carried out in order to obtain the amount of Ru and organic matter, respectively, present on the NPs. The results obtained (Table S1) were in good agreement with the amount of the Ru precursor and bpy ligand added during the synthesis. The percentage of N is used to calculate the amount of the bpy ligand. The remaining weight percentage of C present in the samples can be assigned to solvent THF molecules coordinated to the NP surface, as previously reported.²⁰ Considering cluster magic numbers and the NP size, the number of Ru atoms can be estimated for each system.²⁶ The relative amount of Ru and ligands can be used to estimate experimental formulae for the Ru-bpy series (Table S2): Ru₁₃(bpy)₁(THF)₂ (Rubpy-0.2eq), Ru₅₅(bpy)₄(THF)₂ (Rubpy-0.1eq), Ru₃₀₉(bpy)₁₀(THF)₁₄ (Rubpy-0.05eq), and Ru₅₆₁(bpy)₁₅(THF)₂₆ (Rubpy-0.025eq).

Owing to the aforementioned passivation procedure applied after NP synthesis, the Ru oxidation state (OS) in the NPs was probed by XPS analysis (Figures 2 and S1). The Ru 3p_{3/2} core level spectrum can be exploited to elucidate the OS of Ru in the materials. A comparison of the Ru 3p_{3/2} spectra from the smallest NPs (Rubpy-0.2eq) and a pristine sample of anhydrous RuO₂ reveals that the binding energy (BE) of the peak for the two systems is almost identical (462.8 eV). For the three larger NPs (Rubpy-0.1eq, Rubpy-0.05eq, and Rubpy-0.025eq), the BE of the Ru 3p_{3/2} signal is centered around 462.1–461.8 eV, which is an intermediate value between the BE found for metallic Ru (461.3 eV) and anhydrous RuO₂ (462.8 eV). Therefore, these NPs must be constituted by a mixture of Ru atoms in the 0 and +4 OS. The relative amount of each OS can be obtained through a quantitative analysis of their O 1s spectrum (Figures 2B,E and S1). Three components can be differentiated in the fitting of these spectra: one component centered at 529.5 eV assigned to an O lattice environment, a second component centered at 530.8–530.7 eV assigned to a hydroxyl group (–OH) environment located at the surface of the NPs, and a third component centered at 532.8–532.7 eV assigned to adventitious C–O pollution, common in XPS measurements, residual THF, and/or adsorbed H₂O. Combining both Ru 3p_{3/2} and O 1s spectra, the ratios between both types of O (–OH, O-lattice) and Ru can be calculated, and these ratios can be used to obtain the experimental OS of the NPs (see Section S1 on the SI for further details). The experimental OS of Ru calculated for Rubpy-0.2eq is +3.6, almost identical to the experimental OS calculated for the pristine RuO₂ sample (+3.8). This suggests that the smallest NPs are essentially

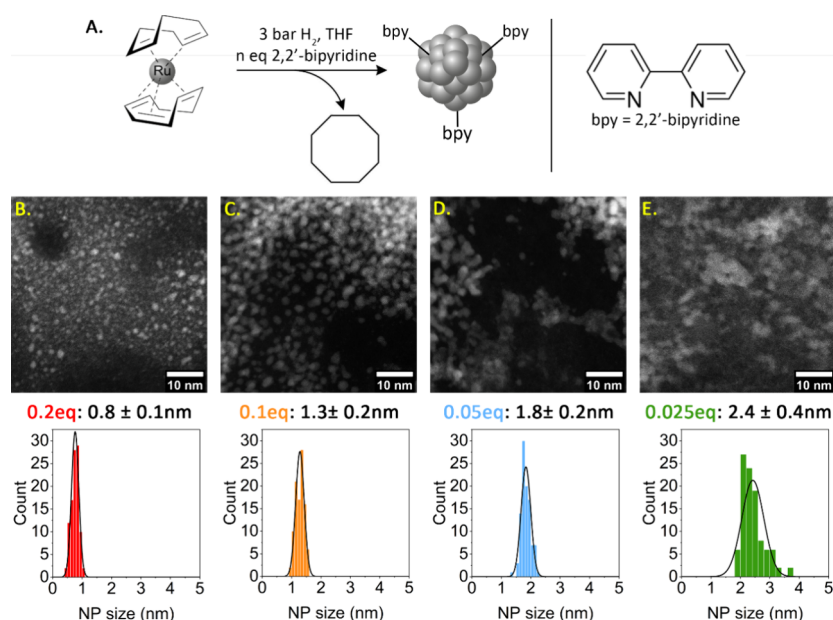


Figure 1. Schematic representation of the organometallic synthesis of bpy-stabilized Ru NPs (A). HAADF-STEM images of the Ru-bpy NPs synthesized with 0.2 (B), 0.1 (C), 0.05 (D), and 0.025 (E) molar equivalents of 2,2'-bipyridine with their respective average size and size distribution.

RuO₂, and most of their Ru atoms are in the +4 OS. In contrast, the experimental OS for **Rubpy-0.1eq**, **Rubpy-0.05eq**, and **Rubpy-0.025eq** is +2, +1.9, and +1.7, respectively (Figure S2). This indicates that **Rubpy-0.2eq** NPs are more prone to oxidation than the largest NPs.

This was further supported by X-ray absorption spectroscopy (XAS). Figure 2G displays the X-ray absorption near-edge structure (XANES) spectra for the Ru-bpy NP series, including RuO₂ and Ru(0) references. Notably, the Ru-bpy NPs prepared with larger amounts of bpy exhibit a progressive shift of the absorption edge towards higher energies compared to Ru(0), indicating a systematic increase in the average oxidation state of Ru from **Rubpy-0.025eq** to **Rubpy-0.2eq**, in agreement with XPS analysis (Figures 2 and S2). This shift in the absorption edge position is consistent with a Ru@RuO₂ core-shell structure with a systematic increase of the NP size from **Rubpy-0.2eq** to **Rubpy-0.025eq**. The smaller the NPs, the larger the number of Ru atoms exposed for oxidation in the sample, thus leading to a higher RuO₂ content. Using the edge position for RuO₂ and metallic Ru(0), the oxidation state of the different systems can be estimated (Figure 2G), obtaining average OS values of +1.7, +1.9, +2.0, and +3.6 for **Rubpy-0.025eq**, **Rubpy-0.05eq**, **Rubpy-0.1eq**, and **Rubpy-0.2eq**, respectively. These OS values closely match the predicted amounts of Ru(0)/RuO₂ by assuming that the outermost layer of atoms of the NPs is oxidized to Ru(+4), and the core atoms remain as Ru(0) (Table S3), thus providing further support for the proposed core-shell structure. The extended X-ray absorption fine structure (EXAFS) spectra shown in Figure 2H provide additional support for this trend by enabling the local atomic environment of Ru to be assessed. The FT spectra of the Ru-bpy systems exhibit peaks at roughly 2.0, attributed to the Ru–O in RuO₂, and 2.7 Å, typical for Ru–Ru interactions in metallic Ru (see Table S4). The R-space experimental spectra were fitted using a simple RuO₂/Ru model by combining both species in the corresponding ratio (Figure S3 and Table S4). The

observed changes in the EXAFS spectra correlate well with the XANES results, supporting the assigned oxidation states.

When performing the electrochemical HER studies with these materials, an activation process is required. It consists of the application of a constant current of -10 mA cm^{-2} for ca. 2 h in order to reduce all of the surface Ru atoms to Ru⁰, which is the active species towards the HER. This can be readily seen by an increase in the slope and a decrease in the overpotential of the polarization curves (Figure 3A) and is in good agreement with our previous work.^{20,27} XAS was used as a tool to evaluate the fate of the catalysts after electrocatalytic turnover and confirm the reduction of the NP surface under negative current. To this end, the Ru-bpy NPs underwent chronopotentiometry (CP) experiments at -10 mA cm^{-2} for 2 h—to generate the active species—and were then frozen in liquid N₂ and stored under an Ar atmosphere until the analyses. XANES analysis revealed a clear shift in the edge position to lower energies for **Rubpy-0.025eq**, **Rubpy-0.05eq**, and **Rubpy-0.1eq**, consistent with a reductive process occurring on the NP surface and overlapping with the fingerprint of metallic Ru (Figure S4). This indicates an effective reduction to Ru(0) during catalysis, which remains on the electrode as the resting active species. Surface reduction was also observed for **Rubpy-0.2eq** under negative current, which reached an average oxidation state of approximately +1.2 (from initial +3.6). The sub-nanometric size of **Rubpy-0.2eq**, being prone to rapid oxidation during sample transfer, prevented its characterization at the pure metallic state. The same trend was observed in XPS analysis under similar conditions (Figure S5). In this case, the **Rubpy-0.2eq** system reached an OS of +0.8 (from initial +3.6 as well), indicating that the time of air exposure during sample transfer affects the NP OS. In view of this, Ru(0) is expected to be the solely resting active species under sustained negative bias in all systems. Finally, analysis of the R-space spectra shows the interconversion of the Ru–O and Ru–Ru peaks, initially observed at approximately 2.0 and 2.6 Å in the Ru(0)/RuO₂ mixtures, to

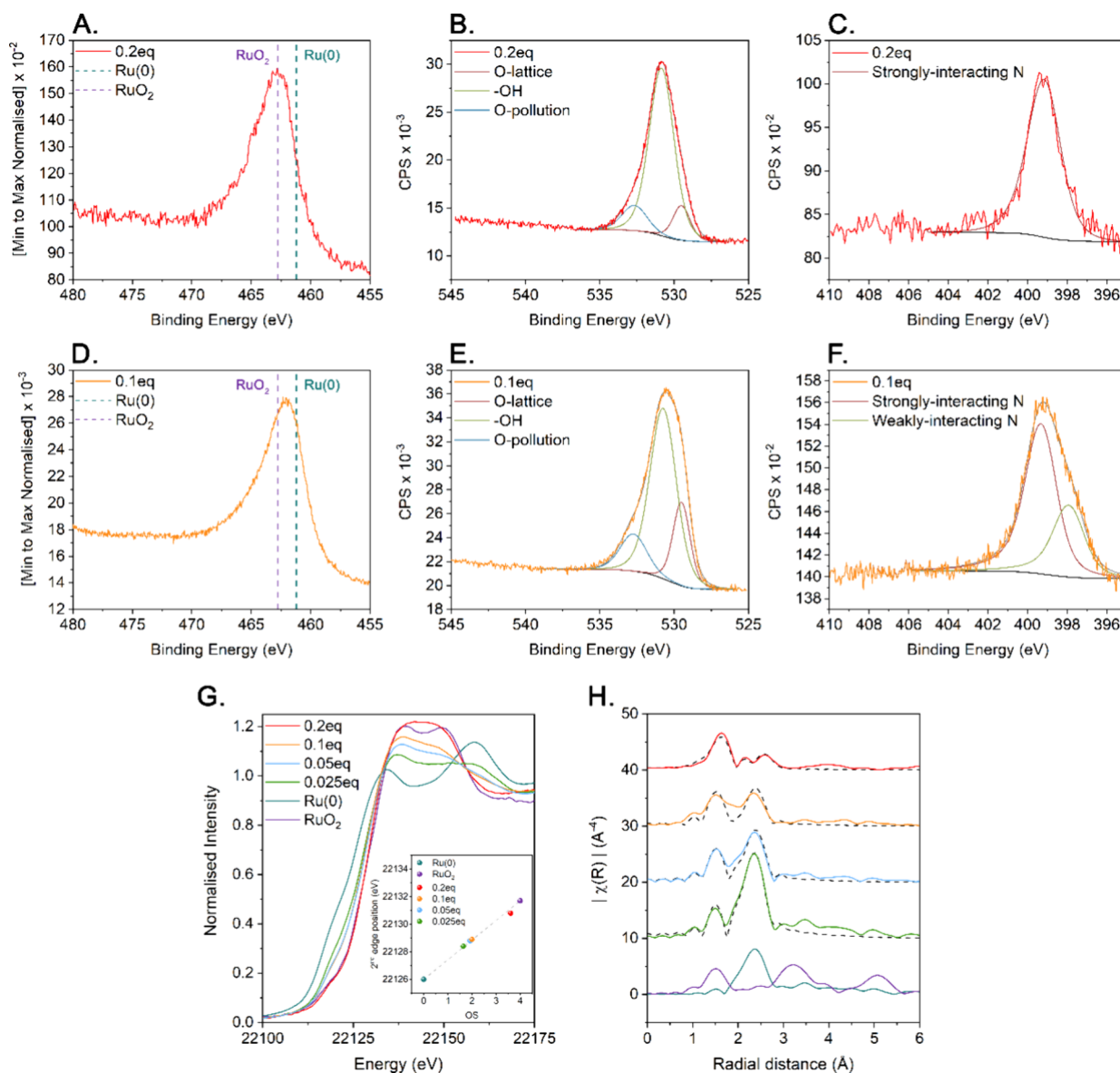


Figure 2. (A) Narrow scan Ru 3p_{3/2} XPS spectrum of **Rubpy-0.2eq** with references of Ru(0) and anhydrous RuO₂. (B) Narrow scan O 1s XPS spectrum of **Rubpy-0.2eq**. (C) Narrow scan N 1s XPS spectrum of **Rubpy-0.2eq**. (D) Narrow scan Ru 3p_{3/2} XPS spectrum of **Rubpy-0.1eq** with references of Ru(0) and anhydrous RuO₂. (E) Narrow scan O 1s XPS spectrum of **Rubpy-0.1eq**. (F) Narrow scan N 1s XPS spectrum of **Rubpy-0.1eq**. (G) Normalized Ru K-edge spectra of **Rubpy-0.025eq**, **Rubpy-0.05eq**, **Rubpy-0.1eq**, **Rubpy-0.2eq**, and Ru(0) and RuO₂ references. Inset: plot of K-edge energy versus oxidation state. (H) Real part of the Fourier transforms of the k³-weighted experimental (solid line) and fitted (dashed line) Ru EXAFS spectra for **Rubpy-0.025eq**, **Rubpy-0.05eq**, **Rubpy-0.1eq**, **Rubpy-0.2eq**, and Ru(0) and RuO₂ references.

metallic Ru in all cases. This further confirms the proposed reductive transformation (Figures S3, S6 and Table S4).

In order to study the surface of the NPs and the interaction between Ru and the bpy ligands in more depth, the samples were analyzed by means of time-of-flight secondary ion mass spectrometry (TOF-SIMS). The mass spectra in positive polarity mode for the four samples **Rubpy-0.2eq**, **Rubpy-0.1eq**, **Rubpy-0.05eq**, and **Rubpy-0.025eq** are similar (Figure S7). The peak centered at $m/z = 101$ has the isotopic pattern of Ru confirming its presence in the materials. The peak centered at $m/z = 157$ is attributed to protonated bipyridine (bpy+H) and evidences the presence of the capping ligand. Importantly, peaks attributed to hydrogenated forms of the ligand (bpy+2H, bpy+4H, or bpy+6H) cannot be observed.

This indicates that the bpy ligand preserves its native chemical structure after coordination to the NP surface despite the H₂ atmosphere used for the synthesis of the Ru-bpy NPs. Finally, the mass spectra provide evidence for an interaction between the bpy ligand and Ru, given that the presence of a peak corresponding to the fragment [Ru(bpy-H)] is observed at $m/z = 257$.

Furthermore, comparison of the N 1s XPS spectrum of a reference Ru complex ([Ru(bpy)₂(qpy)]²⁺; bpy = 2,2'-bipyridine, qpy = 4,4':2,2':4''':4'''-quarterpyridine) with those of **Rubpy-0.2eq**, **Rubpy-0.1eq**, **Rubpy-0.05eq**, and **Rubpy-0.025eq** allowed us to gain insight into the coordination mode of the bpy ligand in the Ru-bpy NPs (Figures 2, S1 and S8). [Ru(bpy)₂(qpy)]²⁺ contains two different types of N, which

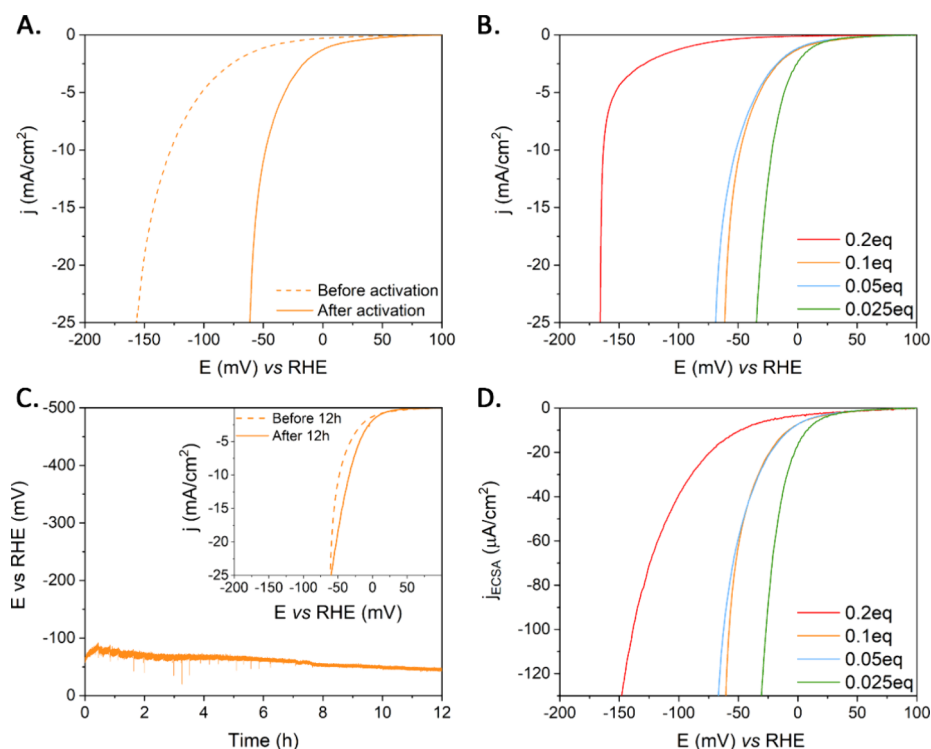


Figure 3. (A) Example of catalyst activation showing the **Rubpy-0.1eq** polarization curves in 1 M H_2SO_4 at the 20 mV s^{-1} scan rate before (dotted line) and after (solid line) 2-h CP at -10 mA cm^{-2} . (B) Polarization curves of activated **Rubpy-0.2eq** (red), **Rubpy-0.1eq** (orange), **Rubpy-0.05eq** (blue), and **Rubpy-0.025eq** (green) in 1 M H_2SO_4 at the 20 mV s^{-1} scan rate. (C) 12-h CP at -10 mA cm^{-2} in 1 M H_2SO_4 using **Rubpy-0.1eq** as an example. *Inset:* the polarization curves before (dotted line) and after (solid line) 12-h CP. (D) Polarization curves of activated **Rubpy-0.2eq** (red), **Rubpy-0.1eq** (orange), **Rubpy-0.05eq** (blue), and **Rubpy-0.025eq** (green) in 1 M H_2SO_4 at the 20 mV s^{-1} scan rate normalized by the electrochemically active surface area.

can be differentiated in the N 1s spectrum (Figure S8): one directly coordinated to the Ru atom appearing at higher BE (from now on referred to as strongly interacting N) and one non-coordinated appearing at lower BE (referred to as weakly interacting N). The N 1s XPS spectra of the **Rubpy-0.2eq**, **Rubpy-0.1eq**, **Rubpy-0.05eq**, and **Rubpy-0.025eq** systems are shown in Figures 2 and S1. The spectrum from the **Rubpy-0.2eq** system can be fitted with only one component centered at 399.1 eV, which is assigned to strongly interacting N according to its BE. On the **Rubpy-0.1eq**, **Rubpy-0.05eq**, and **Rubpy-0.025eq** NPs spectra, the signal can be fitted with two components. Based on the information extracted from the N 1s core level spectrum from complex $[\text{Ru}(\text{bpy})_2(\text{qpy})]^{2+}$, the first component centered at 399.4–399.3 eV can be assigned to strongly interacting N and the second component centered at 397.9 eV can be assigned to weakly interacting N. These strongly and weakly interacting N have been associated with the coordination modes of the bpy ligand: strongly interacting N is assigned to σ coordination through the nitrogen atoms, and weakly interacting N is associated to π coordination through the aromatic framework (Figure S8 and Table S5). The proposed correlation between the different coordination modes and BE values is supported by DFT, as will be discussed in the corresponding section (vide infra). In addition, the coordination of the bpy ligands in reduced Ru-bpy NPs was also investigated. N 1s spectra recorded after catalysis show a poor signal-to-noise ratio, as the NPs are drop-casted onto FTO electrodes. Hence, the substrates dominate the XPS signal and the

low N content appears extremely weak. Nonetheless, insights into the coordination of bpy on Ru(0) NPs can instead be obtained from as-synthesized samples, i.e., before passivation (Figure S9). The Ru(0) OS could not be fully preserved, most likely due to brief air exposure during sample transfer. This is supported by the fact that larger **Rubpy-0.025eq** NPs retain a higher fraction of metallic Ru than the smaller **Rubpy-0.2eq** ones, where more Ru atoms are surface-exposed. Notably, the N 1s signals are almost identical for passivated (Figures 2, S1 and Table S5) and non-passivated (Figure S9 and Table S6) NPs, indicating that the coordination mode of the bpy ligands is independent of the average OS of Ru. In conclusion, narrow-scan N 1s spectra reliably define bpy coordination on catalytically relevant reduced Ru NPs and provide a key input for designing *quasi*-realistic computational models of the synthesized nanomaterials.

The electrocatalytic activity of the four Ru-bpy NP systems towards the HER was then evaluated in 1 M H_2SO_4 . The samples were dispersed in THF and drop-casted onto a glassy-carbon rotating disk electrode (GC-RDE), which was used as the working electrode (WE) in a three-electrode configuration cell. The reference electrode (RE) used was Ag/AgCl (saturated KCl), and a Pt mesh was employed as the counter electrode (CE). A summary of relevant physicochemical data and electrochemical benchmarking parameters can be found in Figure 3 and Table 1.

Prior to recording the polarization curves, the Ru-bpy NPs were activated by reducing the RuO_2 passivation layer to

Table 1. Relevant Physicochemical Data and Electrochemical Parameters of the Ru-bpy Systems Described in This Work

System	NP size (nm)	η_{10} (mV)	ECSA (cm^2)	b (mV dec^{-1})	$j_{\text{ECSA}} (\eta = 50 \text{ mV})$ ($\mu\text{A cm}^{-2}$)	$\log j_0$ (A cm^{-2})
Rubpy-0.2eq	0.8 ± 0.1	164	6.4	39.3	43	−6.22
Rubpy-0.1eq	1.3 ± 0.2	45	35.1	23.6	71	−4.21
Rubpy-0.05eq	1.8 ± 0.2	47	31.7	33.6	66	−3.67
Rubpy-0.025eq	2.4 ± 0.4	21	28.8	32.9	352	−2.66

Ru(0) by means of a CP at -10 mA cm^{-2} , until maximum activity was reached.^{20,27,28} The linear sweep voltammetry (LSV) plots of the activated systems are displayed in Figure 3B. The benchmarking overpotential needed to reach a current density of -10 mA cm^{-2} (η_{10}) for the smallest system (Rubpy-0.2eq, 164 mV vs RHE) is quite large, especially when compared to the low η_{10} achieved for the larger systems (45, 47, and 21 mV vs RHE for Rubpy-0.1eq, Rubpy-0.05eq, and Rubpy-0.025eq, respectively), which are on par with state-of-the-art Ru-based HER catalysts and even with commercial Pt/C in the case of Rubpy-0.025eq (see Table S7). This result is counterintuitive, as the surface per volume ratio increases when decreasing the NP size, which typically translates into a larger number of active sites. Thus, higher catalytic activity should be expected for Rubpy-0.2eq NPs (0.8 nm), rather than Rubpy-0.025eq NPs (2.4 nm).^{7,17,29} The HER kinetics were studied by Tafel analysis of the polarization curves (Figure S10). The measured Tafel slopes are quite low for all systems, around 30 mV dec^{-1} (Table 1), and comparable to commercial Pt/C (32 mV dec^{-1} , Table S7).

In order to rule out changes in the available surface area as the source of the observed trends in the Ru-bpy NPs, measurements of the electrochemically active surface area (ECSA) were carried out following the procedure reported by Jaramillo and co-workers (Table 1, Figures S11, S12 and Section S2).³⁰ The obtained values of 6.4 (Rubpy-0.2eq), 35.1 (Rubpy-0.1eq), 31.7 (Rubpy-0.05eq), and 28.8 cm^2 (Rubpy-0.025eq) were used to calculate the specific current density (j_{ECSA}) (Table 1, Figure 2D). At $\eta = 50 \text{ mV}$, the Rubpy-0.2eq system has a j_{ECSA} of $-11 \mu\text{A cm}^{-2}$, lower than the values obtained for Rubpy-0.1eq ($-63 \mu\text{A cm}^{-2}$) and Rubpy-0.05eq ($-59 \mu\text{A cm}^{-2}$) and significantly less active than the largest system (Rubpy-0.025eq, $-345 \mu\text{A cm}^{-2}$). This indicates that the Rubpy-0.2eq NPs do not only present a lower number of electroactive sites, but the intrinsic activity of these sites is lower than those of the larger Ru-bpy NPs, in good agreement with the trends observed in their overpotentials. The Faradaic efficiency (FE) was measured to investigate the selectivity of the process. No noticeable differences could be spotted as all of the Ru-bpy NPs presented an FE over 99% (Figure S13), confirming the production of H_2 as the only reaction taking place.

Together with kinetic data, the stability of the systems under HER turnover conditions is a critical aspect for practical applicability and was also evaluated. The four electrodes were held at a constant current density of $j = -10 \text{ mA cm}^{-2}$ in a current-controlled experiment for 12 h, and LSV curves were recorded before and after this process (Figures 3C and S14). In all cases but Rubpy-0.025eq NPs, no significant increase in the recorded overpotential was observed, and similar LSV polarization curves were obtained before and after electrocatalytic turnover. For the Rubpy-0.025eq NPs, the overpotential could not be stabilized for long times due to a lower mechanical stability at the electrode surface compared to its counterparts. By

stopping the bulk electrolysis and manually removing the bubbles on the electrode every 30 min, the overpotential of Rubpy-0.025eq could be stabilized for at least 3 h (Figure S14C). This shows that the low mechanical stability likely arises from a weaker interaction between these NPs and the GC electrode, which makes them more prone to be detached upon formation of H_2 bubbles, suggesting that π – π interactions between the aromatic ligands and the GC electrode may play a role in the anchoring strength of these NPs to the electrode surface. In addition, Rubpy-0.2eq and Rubpy-0.1eq were selected as representative systems to be analyzed in TEM after both electrochemical activation (2 h) and long-time bulk electrolysis (12 h). The NPs were drop-casted onto FTO electrodes, and CP at a current of -10 mA cm^{-2} was performed. The samples were then recovered from the electrode surface, redispersed in THF, and drop-casted onto a TEM grid. HAADF-STEM images show that the size and morphology of the NPs did not change in either case. Moreover, EDX analysis confirmed the presence of N on the Ru NPs even after 12 h under catalytic turnover, proving that the ligand is still present after the electrolysis and stabilizing the size and morphology of the NPs (Figures S15–S18).

To shed more light on the root of the inferior specific HER electroactivity of the smallest Rubpy-0.2eq NPs, the available compositional and spectroscopic data were used to build *quasi*-realistic DFT models. The Rubpy-0.1eq system was selected as an example of larger NPs for the sake of balance between computational cost and meaningful comparison, being its catalytic activity representative of all of the largest NPs. The studies have been carried out using the Yang and Saidi electrochemical model,³¹ which combines exchange current densities (j_0), volcano plots, DFT-calculated ΔG_{H^*} , the experimental cathodic transfer coefficient (α), and Volmer–Heyrovsky pathways. From a practical point of view, as we demonstrated in a recent publication,²⁸ it allows direct correlation between the DFT-calculated ΔG_{H^*} values for each surface hydrogen atom on the NP and the local theoretical electrochemical activity, quantified by the theoretical j_0 . The employed organometallic synthetic approach yields NPs of remarkable cleanliness and compositional simplicity. These systems comprise only metal atoms, hydrides, ligand molecules, and solvent molecules (if they have coordinative ability), enabling the NP composition used in the models to be inferred reliably from the available experimental data. Moreover, the two possible coordination modes of the bpy ligand(s) at the NP surface—namely σ -coordination through the nitrogen lone electron pairs to form a chelate or π –aromatic interactions with the metal surface—can be assigned from N 1s XPS data (vide supra, Figures 2, S5, S9 and Table S6). Importantly, the ligand coordination mode is unaffected by the average oxidation state of the NP (XPS of passivated and non-passivated samples, Tables S5 and S6), and analyses by TEM and EDX confirm that both the NP size and the surface-bound ligand are preserved following electrochemical activation (Figures S15–S18). Together, these

observations support the view that the proposed models closely represent the structure of the active catalysts under electrocatalytic turnover.

To build the models, the number of Ru atoms has been calculated based on the NP size (HRTEM, Figure 1) and considering cluster magic numbers, namely, 13 and 55 (see Section S3 in the SI).²⁶ In addition, 1.3 hydrides per surface Ru atom have been added on these NPs in agreement with typical values for this kind of NPs.²⁴ The number of bpy and THF molecules present at the NP surface has been inferred from elemental analysis (Table S2). The composition of the final models assigned to the NPs is $\text{Ru}_{13}\text{H}_{15}(\text{bpy})_1(\text{THF})_2$ for **Rubpy-0.2eq** and $\text{Ru}_{55}\text{H}_{53}(\text{bpy})_4(\text{THF})_2$ for **Rubpy-0.1eq**, as aforementioned.

The smallest NPs (**Rubpy-0.2eq**) contain only one bpy molecule per Ru NP. Its N 1s XPS spectrum can be fitted with only one component, which corresponds to σ -coordinated bpy according to the value of the BE of the peak (Figures 2 and S9). To verify this, two models were made: one with the bpy in σ coordination mode (Figure 4A) and another one with the bpy coordinated in π mode (Figure 4B). The model with σ -coordination shows a calculated adsorption energy (ΔE_{ads}) of $-59.9 \text{ kcal mol}^{-1}$, whereas the calculated ΔE_{ads} for the NP with π -coordination is $-24.5 \text{ kcal mol}^{-1}$. Moreover, Figure 4B shows that the NP surface is not large enough to accommodate a bpy ligand in π -coordination, which results in the cleavage of a Ru–Ru bond and the destabilization of the system. These results are in good agreement with the XPS data, therefore supporting the relationship between N 1s XPS and the assigned bpy coordination modes. Thus, the model for the **Rubpy-0.1eq** NP, which contains 4 molecules of the bpy ligand, was built according to its N 1s XPS spectrum (Table S6). The signal for these NPs can be fitted with both σ - (61%) and π -to-metal coordination (39%). In this way, the model was built with 4 molecules of bpy, 3 in σ -coordination and one in π -coordination mode (Figure 4C).

These models were then used to calculate the ΔG_{H^*} . In previous studies, we found that hydrides in different sites of the NP can have different ΔG_{H^*} values depending on their distance to the Ru coordinated to the ligand.²⁸ In this way, three types of hydrides were studied (Figure S19A): H adsorbed onto Ru coordinated to bpy ($\text{H}^*\text{Ru}_{\text{bpy}}$); H adsorbed onto Ru coordinated to THF ($\text{H}^*\text{Ru}_{\text{THF}}$); and H bound to Ru further away from ligands (H^*Ru). For **Rubpy-0.2eq**, a local effect is indeed observed for the different hydrides, as the calculated ΔG_{H^*} for $\text{H}^*\text{Ru}_{\text{bpy}}$ is $-9.8 \text{ kcal mol}^{-1}$, in contrast with the values of -13.0 and $-13.8 \text{ kcal mol}^{-1}$ calculated for $\text{H}^*\text{Ru}_{\text{THF}}$ and H^*Ru , respectively (Figure 4D). Interestingly, the coordination of THF molecules onto the Ru surface does not affect the ΔG_{H^*} , supporting the choice of this weak σ -donor solvent for the synthesis.²¹ The energy of the Ru–H bond on these NPs is notably large. The hydrogen atoms are bound too strongly to the surface of the NP, and so, this can explain the poor performance of this nanocatalyst for the HER. As shown in Figure S20, the average coordination number (CN) of surface atoms in ultra-small NPs, such as the Ru_{13} model, is significantly lower than that of surface atoms in larger NPs. While adsorption energies and catalytic properties are influenced by global electronic delocalization in transition metal NPs, the local CN remains a relevant descriptor for binding affinity.³² In this case, the low CN of all surface atoms of the Ru_{13} NP (CN = 6) contributes to the excessively strong Ru–H bond, thereby explaining the diminished activity of the smallest NPs.

In contrast, four different hydrides can be differentiated for the **Rubpy-0.1eq** NP (Figure S19B): $\text{H}^*\text{Ru}_{\text{THF}}$ and H^*Ru as in the smaller NP; in this case, two types of hydrides bound to Ru coordinated to bpy can be differentiated, i.e., hydrides bound to Ru coordinated to bpy in σ -coordination ($\text{H}^*\text{Ru}_{\sigma\text{-bpy}}$) and hydrides bound to Ru coordinated to bpy in π -coordination ($\text{H}^*\text{Ru}_{\pi\text{-bpy}}$). Differences in the calculated ΔG_{H^*} for the different environments are found in this system

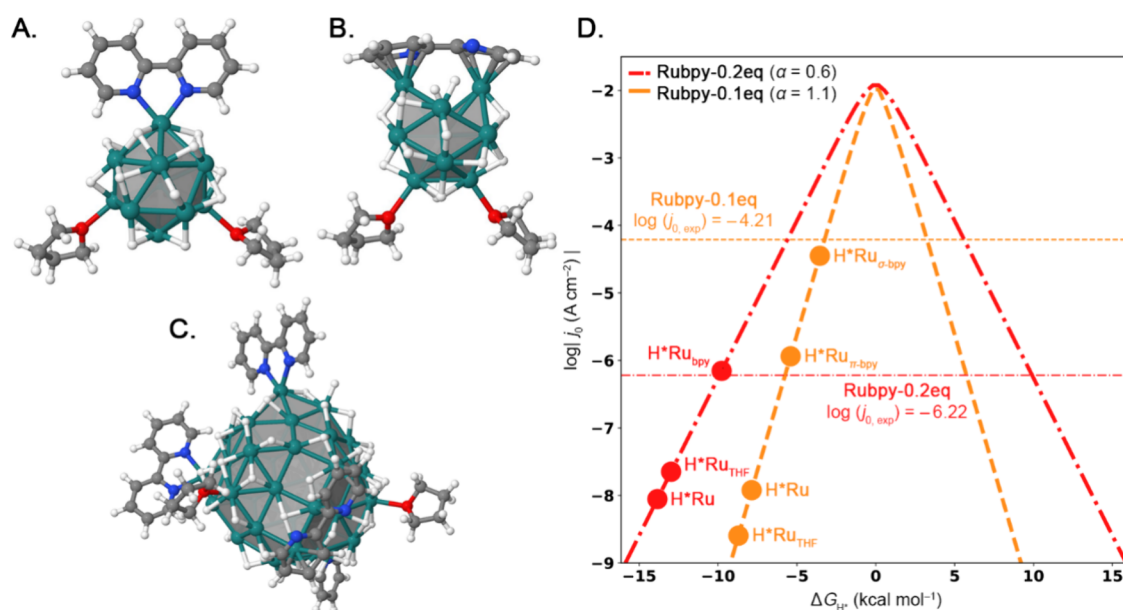


Figure 4. (A) Model of the $\text{Ru}_{13}\text{H}_{15}(\text{bpy})_1(\text{THF})_2$ NP with σ -coordinated bpy. (B) Model of the $\text{Ru}_{13}\text{H}_{15}(\text{bpy})_1(\text{THF})_2$ NP with π -coordinated bpy. (C) Model of the $\text{Ru}_{55}\text{H}_{53}(\text{bpy})_4(\text{THF})_2$ NP. (D) Volcano plot representing the $\log j_0$ as a function of the DFT-calculated ΔG_{H^*} of different sites for **Rubpy-0.2eq** (red) and **Rubpy-0.1eq** (orange). The dotted horizontal lines show the experimentally measured $\log j_0$ (Figure S10A). The slope of the volcano depends on the experimental value obtained for α (Figure S10B).

as well. $\text{H}^*\text{Ru}_{\sigma\text{-bpy}}$ presents a lower ΔG_{H^*} value ($-3.5 \text{ kcal mol}^{-1}$) than $\text{H}^*\text{Ru}_{\pi\text{-bpy}}$ ($-5.4 \text{ kcal mol}^{-1}$). These calculations demonstrate that the coordination mode of the bpy ligand affects the Ru–H bond energy, making the sites close to σ -coordinated ligands more active. In addition, the energies of $\text{H}^*\text{Ru}_{\text{THF}}$ ($-8.7 \text{ kcal mol}^{-1}$) and H^*Ru ($-7.9 \text{ kcal mol}^{-1}$) are also significantly larger than that of hydrides close to ligands. However, in all cases, the ΔG_{H^*} calculated for **Rubpy-0.1eq** is less negative than the ΔG_{H^*} of **Rubpy-0.2eq**, which is in good agreement with the experimentally observed trend (Figure 4D). In addition to the ΔG_{H^*} , it can be seen how only the calculated j_0 of certain types of hydrides ($\text{H}^*\text{Ru}_{\text{bpy}}$ for **Rubpy-0.2eq** and $\text{H}^*\text{Ru}_{\sigma\text{-bpy}}$ for **Rubpy-0.1eq**) matches the experimentally measured one. This suggests that these hydrides, which are highly active towards the HER, represent the major contributors to the observed catalytic activity.

3. CONCLUSIONS

In this work, we report a series of ligand-functionalized Ru nanoparticles with precisely tunable sizes controlled by the amount of 2,2'-bipyridine used as the stabilizer. Their evaluation as HER electrocatalysts demonstrates a clear size–activity relationship. Counterintuitively, the smallest NPs exhibit the lowest activity, whereas the largest NPs deliver the best performance, reaching activity comparable to that of commercial Pt/C. Most importantly, this study provides the first direct evidence that not only the size and presence of ligands have an effect on HER performance, but also the ligand coordination mode can govern the intrinsic HER activity of specific catalytic sites on metal nanoparticles. By combining detailed compositional, spectroscopic, and electrochemical characterization with theoretical studies, we have established *quasi*-realistic computational models that enable deeper insight into these systems. In this context, we propose the elucidation of the ligand coordination modes *via* analysis of N 1s XPS spectra. DFT calculations using the Yang and Saidi electrochemical model reveal that the low activity of the smallest NPs (**Rubpy-0.2eq**) originates from unfavorable ΔG_{H^*} values. For the larger **Rubpy-0.1eq** NPs, our study shows that the bpy coordination mode— σ -coordination via N lone pairs versus π -interaction through the aromatic framework—modulates the ΔG_{H^*} of Ru sites bound to the bpy and thus their HER activity. Notably, only Ru sites coordinated to bpy in σ -coordination display calculated $\log j_0$ values consistent with experiments, indicating that these sites are the primary contributors to the observed catalytic performance. This establishes coordination mode as a decisive and previously underappreciated descriptor of HER performance in ligand-stabilized nanocatalysts. Overall, this work uplifts ligand coordination from a structural detail to a catalytic design parameter. The combined experimental–theoretical strategy presented here provides a robust framework for resolving site-specific reactivity in complex nanomaterials. More broadly, our findings open a new path for catalyst design in which controlling ligand binding modes enables the rational design of highly active sites, moving beyond size and composition as the primary optimization variables.

4. EXPERIMENTAL SECTION

4.1. Reagents

The syntheses of Ru-bpy NPs were carried out under an inert Ar atmosphere alternating between a vacuum line and a glovebox (MBRAUN). The operations entailed were performed using standard Schlenk flasks,

Fisher–Porter tubes, and vacuum-line techniques. The THF and hexane used were purchased from Scharlab. THF was distilled from sodium/benzophenone and hexane from calcium hydride. Both solvents were degassed via freeze–pump–thaw cycles in order to be obtained anhydrous and with high purity. The 2,2'-bipyridine ligand was purchased from Sigma-Aldrich and used as received. The organometallic ruthenium precursor $[\text{Ru}(\text{cod})(\text{cot})]$ was purchased from NanoMePS.

4.2. Synthesis of Ru-bpy NPs

A solution of 2,2'-bipyridine (0.7 mg for **Rubpy-0.025eq**, 1.5 mg for **Rubpy-0.05eq**, 3.0 mg for **Rubpy-0.1eq**, and 6.0 mg for **Rubpy-0.2eq**) in 60 mL of dried THF was added to a pre-dried Fisher–Porter containing 60 mg of $[\text{Ru}(\text{cod})(\text{cot})]$ in a cooling bath of ethanol/liquid N_2 . The mixture was then pressurized with 3 bars of H_2 for ca. 15 min at room temperature under agitation. The suspension turned from yellow into black and was left overnight under stirring. Approximately half of the solvent was removed under vacuum, and the nanoparticles were washed three times with dried hexane, which caused the sedimentation of the nanoparticles as a black powder. The hexane was then removed, and the nanoparticles were redispersed in THF and dried under vacuum. A closed vial containing the NPs under argon was exposed to slow diffusion of air for 4 weeks to passivate the samples.

4.3. Transmission Electron Microscopy

TEM analysis was used to study the NP size, size distribution, and morphology. ImageJ software was used to measure the particle dimensions and calculate the statistical size distribution and the average size. TEM samples were prepared by depositing one drop of the NP dispersion obtained after the synthesis onto a carbon-covered copper grid. TEM measurements were performed on a Jeol JEM 1400 operating at 120 kV with a point resolution of 0.4 nm at the Microscopy Service of the Autonomous University of Barcelona. Atomic resolution STEM-HAADF imaging and EDX mapping were acquired at the Joint Electron Microscopy Centre at ALBA (JEMCA) in a double-corrected Thermo Fisher Scientific Spectra 300 (S)TEM operated at 300 kV using a convergence angle of around 20 mrad. EDX maps were generated using the Cliff–Lorimer methodology. Prior to observation, samples were cleaned using a Gatan Solarus II plasma cleaner in an oxygen atmosphere for 4 cycles of 20 s at 10 W.

4.4. Time-of-Flight Secondary Ion Mass Spectrometry

TOF-SIMS analysis was carried out using a TRIFT V nanoToF II (Physical Electronics, Chanhassen, MN, US) equipped with a 30 kV Bi-LMIG. All mass spectra were acquired at room temperature using the same experimental conditions. Mass spectra were measured in the “bunched” mode, which allows for the best mass resolution. The LMIG gun was tuned to deliver Bi_3^{++} cluster primary ions with a DC current of 12 nA over a 200 μm raster size. The mass range was fixed between 0 and 2000 amu, and the number of frames recorded was controlled to avoid exceeding the static limit (dose $< 10^{13}$ ions cm^{-2}). The dual beam (15 eV e^- /10 eV Ar^+) charge compensation system was used for all analyses. The samples in the form of powder were pressed with a spatula on double-sided adhesive tape in order to prevent electric contact with the sample holder and, thus, differential charging effects. Data processing was performed using ToF-DR software provided by Physical Electronics. All positive polarity mass spectra were calibrated using CH_3^+ ($m/z = 15.0235$), C_2H_2^+ ($m/z = 26.0156$), and Ru^+ ($m/z = 101.9043$) peaks.

4.5. XPS

The XPS analysis was carried out with a PHI QUANTES instrument using a monochromatic Al K α source ($h\nu = 1486.7 \text{ eV}$, power of 50 W). The base pressure during spectra acquisition was better than 1×10^{-9} mbar. The instrument work function was calibrated to give

a binding energy of 83.96 eV for the Au 4f_{7/2} line for metallic gold. The powdered Ru metal, RuO₂, and nanoparticle samples were mounted on the sample holder using Scotch double-sided tape to prevent electrical connection between the sample and spectrometer analyzer. The flood gun system of the spectrometer under standard conditions was used to neutralize the surface and avoid differential charging effects during measurements.³³ All of the spectra were acquired using a 200 μm spot for the X-ray beam. Survey spectra were recorded with a pass energy of 280 eV and an energy step of 1 eV. Core level spectra were acquired with a pass energy of 55 eV and an energy step of 0.05 eV. Sample damage during measurement was checked by comparing initial fast scan XPS core level spectra with the corresponding long acquisition time spectra discussed in the manuscript. No sign of degradation was detected. Data treatment was carried out with CasaXPS Version 2.3.27PR1.5.³⁴ XPS spectra from pristine RuO₂, Rubpy-0.2eq, Rubpy-0.1eq, Rubpy-0.05eq, and Rubpy-0.025eq samples were calibrated by establishing at 529.5 eV the peak assigned to O-lattice in the O 1s core level spectra.³⁵ The validity of this calibration procedure was confirmed through the valence spectrum of the samples in which the Fermi edge is aligned at 0 eV in binding energy after calibration as a consequence of the electronic conducting character of the Ru metal and RuO₂. XPS spectra from the Ru metal were directly calibrated by aligning the Fermi level at 0 eV in the valence band spectrum. Shirley background was used in all of the core-level spectra. Fitting of the spectra was accomplished by the use of components based on Voight functions and LF line shapes, as implemented in CasaXPS.

4.6. Elemental Analysis and ICP-OES

Elemental analysis and ICP-OES were carried out at the Chemical Analysis Service from the Autonomous University of Barcelona on a Flash EA 2000 CHNS from Thermo Fisher Scientific and an Agilent 5900 spectrophotometer, respectively.

4.7. NP Formulae Calculation

The number of bpy molecules was inferred from the N wt % obtained by elemental analysis. The remaining C wt % was attributed to the presence of THF molecules. The amount of Ru was obtained from ICP-OES and was in good agreement with the remaining wt % after subtracting the amount of organics from elemental analysis. In this way, Ru/bpy and Ru/THF molar ratios were calculated. The number of Ru atoms per NP was estimated with cluster magic numbers. For Ru hcp, 0.8 nm (Rubpy-0.2eq), 1.2 nm (Rubpy-0.1eq), 1.8 nm (Rubpy-0.05eq), and 2.4 nm (Rubpy-0.025eq) correspond to one, two, four, and five layers of atoms around the Ru core, respectively. Thus, a Ru₁₃ cluster was attributed to Rubpy-0.2eq, a Ru₅₅ NP to Rubpy-0.1eq, a Ru₃₀₉ NP to Rubpy-0.05eq, and a Ru₅₆₁ NP to Rubpy-0.025eq.²⁶ The empirical formulae estimated for each system can be found in Table S2.

4.8. Electrochemical Measurements

The experiments were performed with an OrigaFlex 01A potentiostat using a KCl-saturated Ag/AgCl electrode as the reference electrode and either a Pt mesh or a Pt rod as the counter electrode. The electrolyte consisted of a solution of 1 M H₂SO₄ (pH = 0) in MiliQ water. The ohmic drop was automatically compensated at 100% by the software. The samples were deposited onto a glassy-carbon rotating disk electrode with an area of 0.2 cm² rotating at 3000 rpm as the working electrode. In the case of the hydrogen-monitored bulk electrolysis, the experiments were carried out in a H-type cell with Ag/AgCl (3 M NaCl) as the reference and a fluorine-doped tin oxide (FTO) electrode containing the sample as the working electrode. All data were converted to the RHE after the electrochemical experiments.

4.9. Electrode Preparation

The electrode ink consisted of a 2 mg mL⁻¹ dispersion of the Ru-bpy NPs in THF. It was prepared by adding 1 mg of sample to 500 μL of distilled THF and sonicating for ca. 20 min until a homogeneous dispersion was formed. Afterwards, 15 μL of ink were drop-casted onto a glassy carbon RDE tip (0.2 cm²) and dried under pressurized air. For the preparation of FTO electrodes, 25 μL of ink were drop-casted in an area of 1 cm² and allowed to dry under air.

4.10. X-ray Absorption Spectroscopy

The Ru K-edge was utilized to conduct measurements on Rubpy-0.025eq, Rubpy-0.05eq, Rubpy-0.1eq, Rubpy-0.2eq, Ru, and RuO₂ in transmission mode. On the other hand, Rubpy-0.025eq, Rubpy-0.05eq, Rubpy-0.1eq, Rubpy-0.2eq after activation were measured on glassy-carbon electrodes in fluorescence mode using a 36-element germanium detector. Spectra were acquired at the SAMBA beamline of the SOLEIL synchrotron, operating with an electron beam current of 450 mA. The incident energy was selected by a Si (200) double crystal monochromator. Incident flux was ca. 1×10^{10} ph s⁻¹ using a beam size of 2×0.5 mm. Powder samples were prepared by diluting the corresponding powder with cellulose in a pellet ($\phi = 6$ mm), followed by placement in the sample holder and sealing with 30 μm Kapton tape. Samples were kept at 80 K in a N₂ LN₂-cryo cryostat. Energy calibration was performed concurrently for each measurement, with each reference metal placed in front of the second ion chamber. Incident energy was calibrated by referencing the inflection point of the corresponding metallic foil, which was 22117.0 eV for Ru. The final spectra were processed and normalized using the Athena program included in the DEMETER package.

4.11. DFT Calculations

The Ru₁₃H₁₅ and Ru₅₅H₅₃ models have been previously reported and discussed.^{20,36} DFT calculations were performed using the Vienna ab initio simulation package (VASP).^{37,38} Spin-polarized calculations employed the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) for the exchange–correlation potential.³⁹ The projector augmented-wave (PAW) method was used for an all-electron-like treatment of core–valence interactions,^{40,41} with PAW datasets for ruthenium including the 4p, 4d, and 5s states (14 valence electrons). A kinetic energy cutoff of 500 eV was applied.⁴² Brillouin zone sampling was limited to the Γ -point.⁴³ Gaussian smearing with a width of 0.02 eV was used to improve convergence. Geometries were optimized until the residual forces on all atoms were below 0.02 eV/Å. Supercells were defined to maintain at least 16 Å of vacuum between periodic images of the metal clusters, resulting in cell dimensions of $27 \times 28 \times 27.5$ Å for Ru₁₃H₁₅(bpy)₁(THF)₂ and $33 \times 36.5 \times 35$ Å for Ru₅₅H₅₃(bpy)₄(THF)₂.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.6c01337>.

Additional graphs, TEM images, and experimental details and methods (DOCX)

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Notes

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ACKNOWLEDGMENTS

X.S. and J.G.-A. thank MINECO/FEDER (PID2019-104171RB-I00) and MICIU (PID2023-146787OB-I00) for financial support. Authors acknowledge financial support from Departament de Recerca i Universitats: del Departament d'Acció Climàtica, Alimentació i Agenda Rural; i del Fons Climàtic de la Generalitat de Catalunya (2023 CLIMA 00011

and 2023 CLIMA 00036). N.R. and K.P. thank CNRS and University of Toulouse. I.d.R. and R.P. thank the CALMIP HCP for generous allocation of computational time (grant P0611) as well as INSA-Toulouse and the University of Toulouse. L.F. thanks MICIU/AEI/10.13039/501100011033 and FEDER, EU (PID2021-128197NA-I00) and El FSE Invierte en tu Futuro (RYC2018-025394-I Fellowship). M.G.-S., O.R., and S.D. acknowledge the Max Planck Society for financial support. G.M. thanks the MICIU for the FPU predoctoral grant (FPU19/04322). M.G.-S. acknowledges the support of the HORIZON-MSCA-2021-PF project TRUSol No. 101063820 and the Agencia Estatal de Investigación (RYC2024-050678-I). XAS experiments were performed at the SAMBA beamline at the SOLEIL Synchrotron under the proposal No. 20221353 with the collaboration of SOLEIL staff. We specially acknowledge Andrea Zitolo (SAMBA at SOLEIL) for their assistance during the XAS experiments. Á.L.-R. thanks AGAUR for the Joan Oró FI grant (2022FI_B 00413). I.L. acknowledges the Bourgogne-Franche-Comté Region and the ANR for financial support through the “ELECTRICALLY” ANER project (2024PRE00037) and the RINTEL-H2 project. Authors acknowledge the use of instrumentation as well as the technical advice provided by the Joint Electron Microscopy Center at ALBA (JEMCA) and funding from Grant IU16-014206 (METCAM-FIB) to ICN2 funded by the European Union through the European Regional Development Fund (ERDF), with the support of the Ministry of Research and Universities, Generalitat de Catalunya.

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