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The role of electronic structure in the hydrogen evolution reaction dynamics as catalyzed by Ru-based complexes

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The development of efficient catalysts for the hydrogen evolution reaction (HER) is of paramount importance in the field of clean energy technology. In this work, we provide a detailed theoretical molecular-level investigation of the catalytic activity of three structurally related ruthenium complexes, by using DFT calculations and molecular dynamics (MD) simulations. The catalytic ability of a di-nuclear complex (**C1**) and two mononuclear analogues (**C2**, **C3**) are examined. Complex **C2** shows a low activation barrier (8.6 kcal mol⁻¹), but H₂ release is kinetically slow compared to **C1**. **C3**, despite having favourable energy pattern, fails to release hydrogen. This reveals that factors beyond simple activation barriers, such as ligand coordination flexibility, are crucial for effective catalysis. Analysis of the LUMO distribution shows a significant anti-bonding character for **C1** and **C2**, i.e. H₂ release. On the contrary H₂ is not involved in the **C3** LUMO, which is mainly of π nature and localized on the ligands. Thus, this work provides a new paradigm for the rational design of HER catalysts based on the LUMO distribution (anti-bonding) analysis in the catalyst transition state, which is relevant to H₂ release.

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1. Introduction

Water electrolysis stands as the primary method for green hydrogen production, making it a key strategy for a sustainable economy powered by renewable energy.^{1–4}

In this field, proton exchange membrane electrolysis cells (PEM-ECs) are recognized as the leading low-temperature (below 100 °C) devices for water electrolysis.^{5,6} They offer significant advantages over alkaline electrolyzers, including high faradaic efficiency, compact design, fast response times,

and the ability to operate at high current densities exceeding 2 A cm⁻².^{7,8} On the other hand, PEM-ECs rely on costly platinum group metals (PGM), specifically platinum and iridium oxide, which serve as catalysts for the hydrogen (HER) and oxygen (OER) evolution reactions in acidic environment.^{5–7,9–12} This limitation has driven the research towards developing alternative heterogeneous electrode materials free of platinum and iridium,^{13–16} or in reducing PGM content, for example through the use of single atoms or organometallic metal complexes.^{7,17,18} Alternatives to PGMs also include enzymes like hydrogenase and nitrogenase or synthetic molecular catalysts.^{15,17} The latter exhibit higher turnover numbers, tuneable properties through organometallic synthesis, and facilitate mechanistic elucidation compared to heterogeneous materials.^{15,17} Enzymes offer extremely high hydrogen evolution efficiencies,^{19,20} but their limited stability in oxygen, narrow pH range stability, sensitivity to temperature, poor electrode contact and low efficiency in large-scale production make them impractical for PEM-ECs.^{21–25}

Several synthetic molecular catalysts are reported, featuring different metals as active sites and various ligands.^{19,26–32} Most of these catalysts operate at neutral pH and behave as hydrogenase-mimicking catalysts. Within this range of compounds, di-nuclear ruthenium complexes have been explored as [Fe–Fe] hydrogenase mimics,^{33,34} yet we found only one example of [Ru–Ru] complex used as an electrocatalyst for water splitting.³⁵ Despite the

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abundance of known electrocatalysts for hydrogen production, very few have been successfully tested in a full PEM electrolyze setup.¹⁷ The most effective results are reported by Dedov *et al.*, who prepared and studied functionalized clathrochelate iron, ruthenium, and cobalt complexes adsorbed on carbon paper.^{36,37} These complexes were used as electro(pre)catalysts for hydrogen production within a PEM membrane electrode assembly (MEA), achieving impressive current densities of over 1200 mA cm⁻² at 2.2 V. However, a crucial challenge remains: these complexes are characterized by chemical instability, leading to a significant drop in current density after one day of operation.³⁷

In a previous paper,³⁸ we studied a novel organometallic [Ru₂(OTf)(μ-H)(Me₂dad)(dbcot)₂] dinuclear Ru–Ru complex (C1) adsorbed onto conductive carbon. A PEM-EC fed with pure water equipped with C1 catalyst showed remarkable chemical stability and high catalytic activity: evolving 28 L of H₂ per gram of ruthenium per minute, with a turnover frequency (TOF) of 7800 mol H₂ per mol of catalyst per hour and remained stable without loss of activity for 7 days. Notably, the TOF of C1 is exceptionally high compared to other reported HER catalysts,³⁹ resulting in a high H₂ production.⁴⁰

In this paper, a theoretical approach is followed to unravel the behaviour and the catalytic mechanism of C1 complex. To study the hydrogen evolution mechanism, we relied on steady-state potential energy surfaces (PES) analysis (determining stationary points as equilibrium reagents, products, intermediate species, and transition states) and *ab initio* molecular dynamics (MD) calculations by using the dynamic reaction coordinate (DRC) algorithm.⁴¹ In addition, the catalytic ability of two different mononuclear Ru complexes, structurally similar to C1, is studied for close comparison.

The purpose of our theoretical study is to establish the fundamental catalyst properties (both metal and ligand-based) that govern the reactivity of Ru complexes, specifically for hydrogen production. Analysis of the LUMO distribution is found to provide a rule for discriminating the capacity to behave as an efficient catalyser. It is found that the analysis of the LUMO distribution, in the catalyst transition state, provides a rule to evaluate the possible efficiency of the catalyst (or its failure).

2. Theoretical calculations

All the theoretical results herein reported are performed in the framework of *ab initio* quantum mechanical based methods, using GAMESS,⁴² and the Gaussian 16⁴³ suite of programs. Unless otherwise stated, all calculations were performed using C1 symmetry and unrestricted wave function. Chemcraft⁴⁴ served for visualizing molecular structures, and *ab initio* molecular orbitals, while MacMolPlt⁴⁵ was used to display DRC trajectories.

Custom Fortran-based codes were developed to extract molecular geometrical parameters from DRC calculations, enabling analysis of angle and bond distance variations over

time (codes are available on request from the author C.F.). For all the structures reported as stationary states shown in the PES *versus* reaction coordinates plot, molecular geometries underwent full optimization at PBE0-D3BJ/def2-SVP/def2-TZVP(Ru) level of theory, then Hessian calculation (vibrational frequency spectra) allowed to ascertain that the optimized geometries were true minima, as all the calculated vibrational frequencies are real-positive for reagents, products, and intermediate species alike. The PBE0-D3BJ/def2-SVP/def2-TZVP(Ru) level of theory was selected for time independent calculations for the sake of close comparison with the results previously reported by Vizza.³⁸

Finally, *ab initio* MD trajectories were calculated within the DRC paradigm by J. P. Stewart as implemented in GAMESS at the PBE0/3-21G level of the theory.⁴⁶ The transition state geometries served as the starting structure in DRC calculations. Two sets of trajectories were computed featuring a molecular total kinetic energy of 5 and 10 kcal mol⁻¹ were compared (see the manuscript text on the strategy underlying this choice).

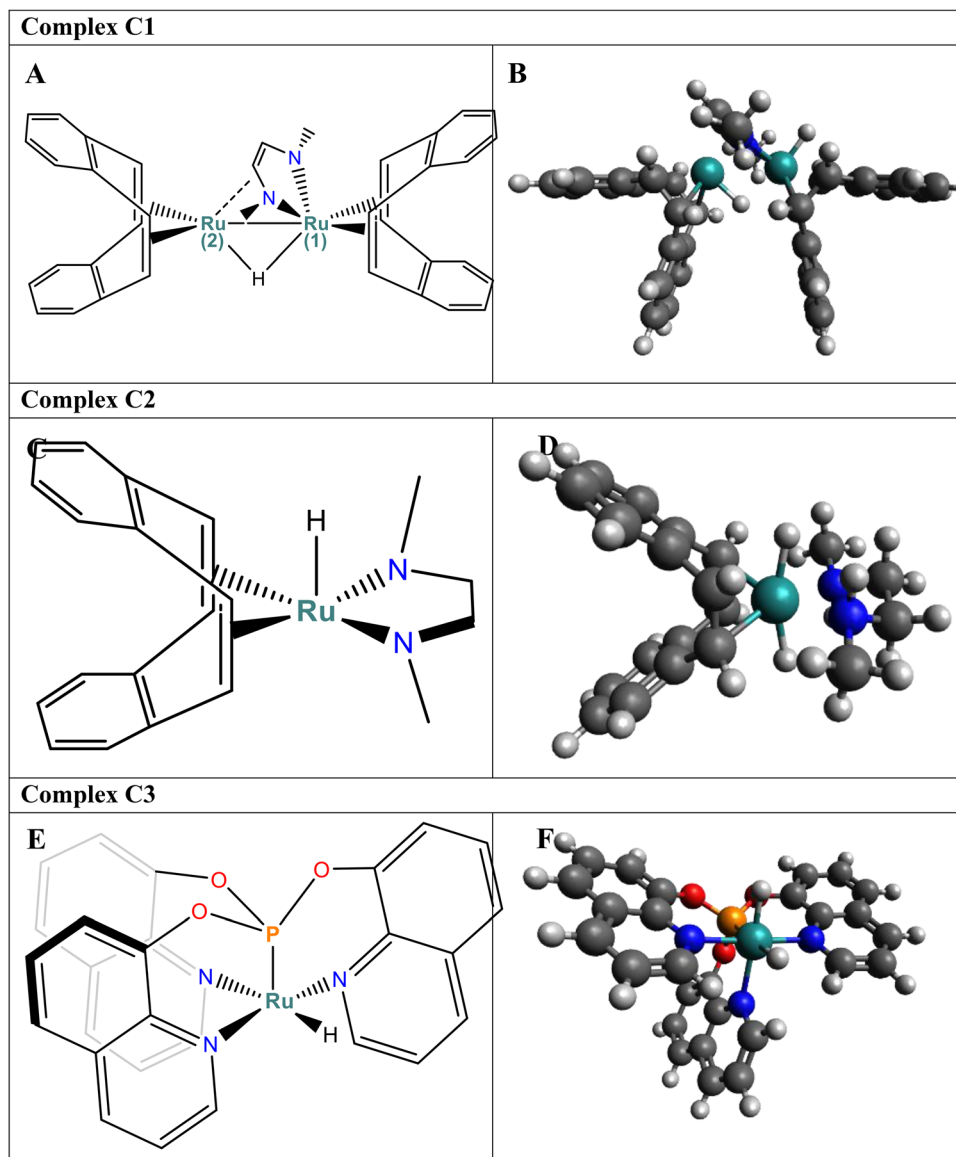
3. Ruthenium catalysts chemical structures

Scheme 1 presents the structures of the three investigated ruthenium-based catalysts. The typical skeletal representations are shown on the left, while the optimized structures of the protonated ruthenium complexes using a ball-and-stick model are reported on the right. The latter represent the second step of the proposed reaction mechanism and are referred to as “input complexes” in the PES (see Section 4.1.1, “Reaction path” for details).

Complex C1 (Scheme 1(A) and (B)) is the dinuclear Ru diazadiene olefin complex [Ru₂(μ-H)(Me₂dad)(dbcot)₂] (where Me₂dad = *N,N'*-dimethyldiazabutadiene and dbcot = dibenzo[*a,e*]cyclooctene). The active site features two ruthenium atoms bridged by a hydride ligand. The Me₂dad moiety chelates one ruthenium atom (Ru1) *via* its nitrogen atoms, while its π-system interacts with the second ruthenium atom (Ru2) atom *via* π-d backbonding. This ligand allows delocalization of the negative charges during the catalyst redox cycle. Each ruthenium atom is also bound to a dibenzo[*a,e*]cyclooctene ligand. This coordination is characterized by backdonation from Ru–Ru unit into the π*-orbitals of the coordinated C=C_{dbcot} bonds.

Complex C2 (Scheme 1(C) and (D)) is a structurally similar analogue of C1; however, its single ruthenium atom makes it a promising alternative to C1, as its synthesis requires less of the expensive ruthenium metal. C2 is characterized by a Ru–dbcot bond and a hydride ligand. Another difference with C1 lies in the completion of its coordination sphere by a different diaza-ligand: *N,N'*-dimethyldiazabutane (Me₂ddbu).

Complex C3 (Scheme 1(E) and (F)) is also a homonuclear ruthenium complex. Here, Ru is coordinated by three nitrogen atoms of three quinoline (Qn) ligands and a hydride ligand. Furthermore, a bridging phosphite group connects the three



Scheme 1 Geometries of ruthenium complexes. On the left: structure of the complexes. On the right: balls and sticks models of the protonated complexes.

Qn ligands *via* P–O–C bridges. The central Ru atom is also formally bound to the phosphorous atom.

4 Results and discussion

4.1 Steady state potential energy surface

4.1.1 Reaction path. In a previous study, we thoroughly investigated the catalytic behavior of complex **C1** for hydrogen evolution.³⁸ A comprehensive reaction mechanism was proposed, leveraging a multi-faceted approach combining experimental insights, data from multi-nuclear NMR spectroscopy, GC-TCD and DFT calculations. This previous work highlighted several crucial aspects of the catalytic activity of **C1**: first, the need for an acidic environment for hydrogen

evolution; second, that protonation occurs selectively at Ru1, and the bridging hydride moiety is a spectator in the process; third, the reaction proceeds *via* a rate-limiting ruthenium reduction step. Interestingly, the **C1** complex supported on a PEM was found to evolve hydrogen even in neutral water, a phenomenon we explained by the ability of the PEM to generate a localized acidic microenvironment in the vicinity of the ruthenium complex.^{6,7}

The reaction mechanism for the HER catalyzed by the three catalysts is schematically presented in Fig. 1(A). The catalytic cycle starts from the reduced form of complex **C1**. The first step involves the protonation of Ru1. In the second step, an oxidative addition occurs: the complex is oxidized, and two hydrogen atoms on the ruthenium surface form a dihydrogen molecule. This H₂ molecule is loosely bound to a water molecule and forms a van der Waals

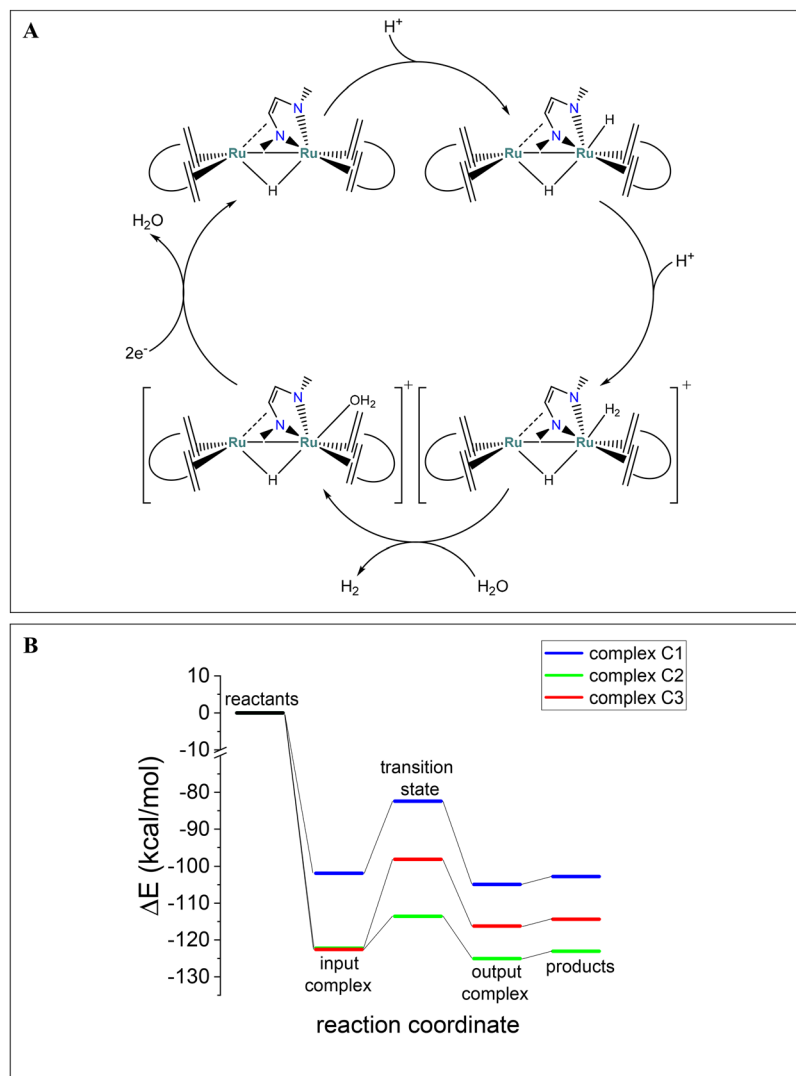


Fig. 1 (A) HER reaction molecular scheme for C1 catalyst, following indications from ref. 38 (B) Potential energy surface versus reaction coordinates plot of the species involved during hydrogen evolution by complex C1 (blue), C2 (green) and C3 (red). Calculations are performed at the PBE0-D3BJ/def2-SVP/def2-TZVP(Ru) level of theory.

complex with an aromatic ring of a dbcot ligand, resulting in a molecular system best described as a hydrated non-classical dihydrogen complex. The third reaction step can be conceptualized as an intramolecular proton transfer from H_3O^+ to the terminal hydride, generating a coordinated and slightly polarized $\text{H}^{\delta-}-\text{H}^{\delta+}$ species, to which the H_2O molecule remains loosely bound *via* an $\text{H}_2\text{O} \cdots \text{H}^{\delta-}-\text{H}^{\delta+}$ hydrogen bridge. The displacement of H_2 from the ruthenium coordination sphere by H_2O constitutes the fourth and last step, followed by a two-electron reduction of the complex, which releases the water molecule and regenerates the starting state. For the three catalysts, we explored the PES relevant to the elementary steps described above, and we calculated the transition state energies at the PBE0/3-21G level of theory. A detailed comparative analysis of their PES profiles is presented in Fig. 1(B). The overall catalytic process is thermodynamically favorable for each complex. The rate-determining step, characterized by the highest activation barrier, is consistently identified as the displacement of

hydrogen from the active site. The calculated Gibbs free energies of activation ($\Delta G^\ddagger$) are 19.5, 8.6 and 24.4 kcal mol⁻¹ for C1, C2 and C3, respectively, which are low enough to enable hydrogen displacement. The optimized geometries of the transition states for each complex are detailed in Fig. 2.

4.1.2 Correlation diagram. Fig. 3 presents the molecular orbital energy correlation diagram for complexes C1, C2, and C3. The diagram highlights the energies of the frontier orbitals—the HOMO and LUMO—as well as other virtual (red bars) and occupied (blue bars) molecular orbitals within the energy window ranging from -2.5 to -10 eV. The HOMO–LUMO energy gap is of particular interest, as it provides a first-order approximation of the stability of a molecule, or, in this case, a complex. A larger gap is generally indicative of greater stability and a lower likelihood of undergoing significant molecular rearrangement such as releasing hydrogen. Analysis of the data reveals that complexes C1 and C3 possess smaller

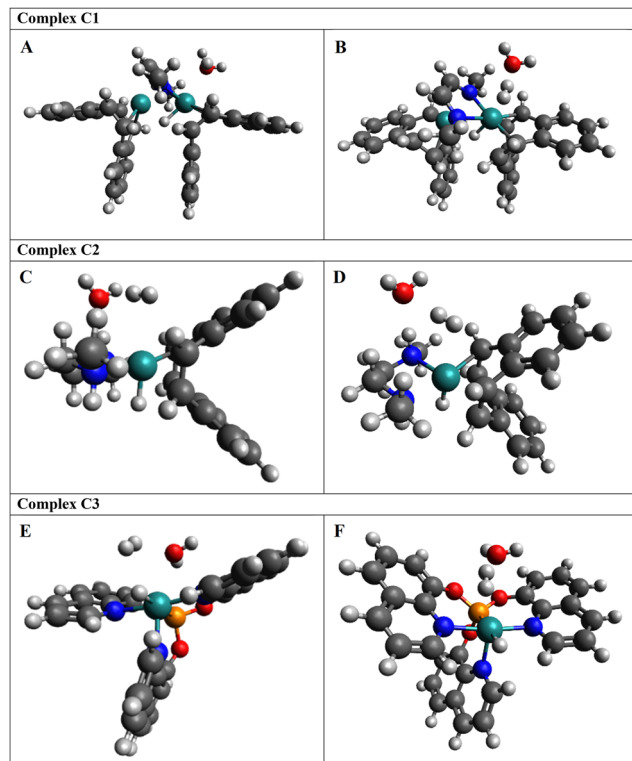


Fig. 2 Transition state geometries highlighting the position of H_2 . On the left: front view. On the right: side view.

HOMO–LUMO energy gaps, approximately 2.5 eV and 1.5 eV, respectively. In contrast, complex C2 exhibits a significantly larger energy gap of about 5 eV. This marked difference in electronic structure suggests that C2 is more stable and less prone to dissociation, which has important implications for its catalytic activity. This correlation between the electronic properties and molecular stability will be explored in greater detail in the following section on molecular dynamics.

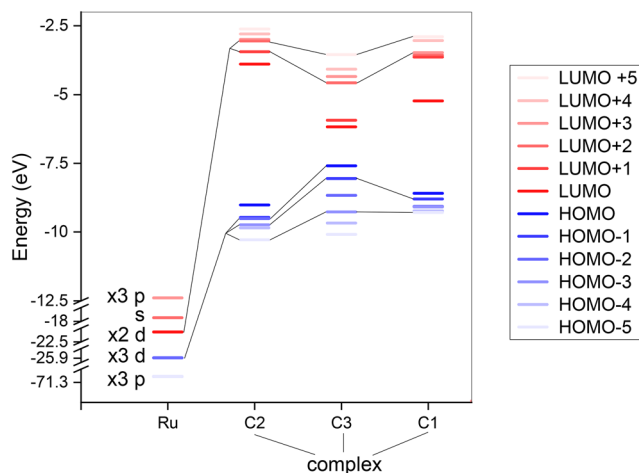


Fig. 3 Molecular orbital energy correlation diagram. On the left the atomic orbital energies of the ruthenium atom are shown, on the right the MO energies from LUMO+5 to HOMO–5 are presented for each complex. The lines connect the d orbitals in each structure.

4.2 Molecular dynamics: dynamic reaction coordinate (DRC)

DRC calculations were performed for each of the three complexes. As the starting point, their respective transition states (Fig. 2) were chosen. For each trajectory, the initial velocity vector was generated by projecting the Hessian matrix (obtained from a preceding calculation at the initial DRC geometry), with the kinetic energy distributed across each normal mode as its zero-point energy. Our analysis of these trajectories focuses on monitoring the time-dependent changes in potential energy, which are expressed through variations in bond lengths, valence angles, interplanar angles, and dihedral angles.

4.2.1 Geometrical variations molecular trajectories. Results from DRC calculation for the C1 catalyst are presented in Fig. 4. We highlight only the key geometrical variations that are crucial for understanding the behaviour of the complex.

Ru–H distance increases over time, indicating the dissociation of hydrogen from the ruthenium centre (Fig. 4(A)). Simultaneously, a water molecule approaches the ruthenium, and after 100 fs, the Ru–H₂O distance shows a sinusoidal periodical pattern typical of a stretching mode, indicating the coordination of the water molecule to the ruthenium atom (Fig. 4(B)). This is consistent with the proposed third step of the reaction mechanism (see Fig. 1(A)).

Following the water molecule coordination, the Ru–Ru bond distance undergoes stretching of a stable chemical bond (Fig. 4(C)) and the Ru–H–Ru angle, centered on the bridging hydride, oscillates around a mean value (Fig. 4(D)). This evidence supports the non-participation of the bridging hydride moiety in the formation of molecular hydrogen.

Finally, the flexibility of the dbcot ligands is assessed. Both the inter-ligand angle (between the two dbcot ligands) and the inter-ring distance (between the two opposing rings, one from each ligand) increase over time (Fig. 4(E) and (F)). This evidence suggests that the ligands are moving apart from one another, while simultaneously moving toward the ruthenium centres. This interpretation is further supported by the decrease in the amplitude of angle between the two axial benzyl rings of dbcot ligands (one for each ligand), centered on one ruthenium atom, over time (Fig. 4(G)). Finally, the time-dependent variation of the angle between the Ru–Ru axis and each individual dbcot ring (Fig. 4(H) and (I)) reveals a typical stretching mode, confirming that both rings contract toward the active site.

The observed geometrical changes did not reveal any direct coordination or significant mechanistic involvement of the Me₂dad ligand with either the ruthenium metal, the dihydrogen molecule, or the incoming water ligand, suggesting its relatively passive role in the reaction mechanism. This implies that its role is predominantly structural, primarily serving to saturate the metal coordination sphere, or providing electronic stabilization through charge compensation.

Like the C1 catalyst, C2 releases hydrogen and subsequently coordinates a water molecule in its place within the ruthenium coordination sphere. However, hydrogen release from C2 occurs more slowly (compare Fig. 5(A), (B) with Fig. 4(A), (B)). After the H–H bond formation (occurring approximately at

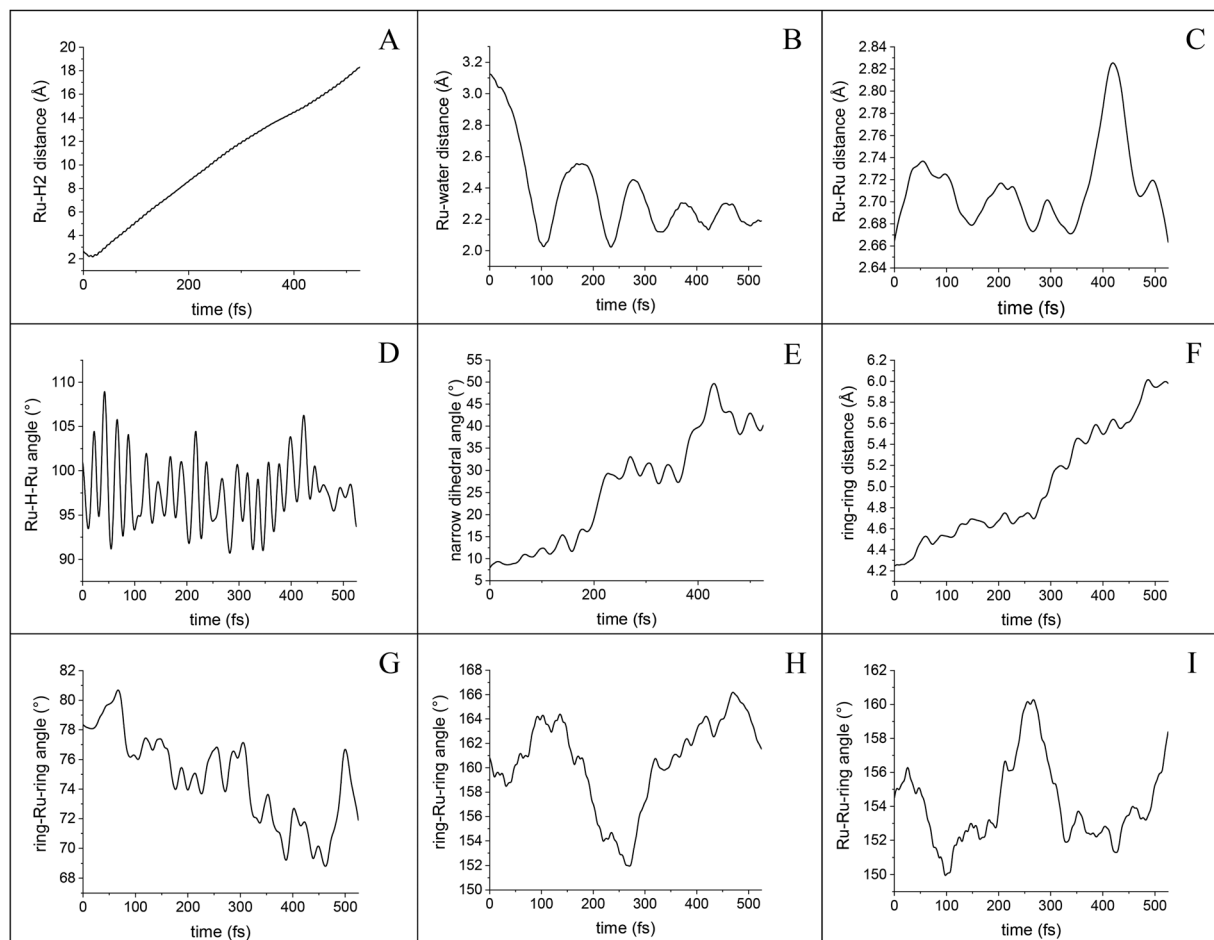


Fig. 4 C1 catalyst intermolecular geometrical parameters as a function of time, DRC calculation performed with 5 kcal mol^{-1} total kinetic energy. Results obtained at 10 kcal mol^{-1} are shown in Fig. S1. (A) distance of the H atom dissociating from Ru. (B) water molecule, Ru distance. (C) Ru–Ru distance. (D) Ru–H–Ru angle. (E) variation in the angle between the two dbcot ligands. (F) variation in the distance between the two dbcot benzyl rings, directly facing each other. (G) and (H): variation in the angle between the axial benzyl ring of one dbcot ligand and the innermost benzyl ring of the other dbcot ligand. Both possible pairs are shown. (I) variation in the angle between the Ru–Ru axis and the dbcot ligand that moves towards the center.

200 fs in C2), the H_2 molecule remains in close proximity to the ruthenium atom (at a distance ranging between 5 to 6 Å), the actual dissociation starts only at a later stage (approximately at 750 fs), as can be observed from the analysis of the distance vs. time pattern in (Fig. 5(A)).

Upon hydrogen dissociation (at 750 fs), the water molecule coordinates the ruthenium atom. This coordination event is accompanied by an increase in amplitude of the angle between the ligands (Fig. 5(C)). Likewise, the angle between the two nitrogen atoms of the Me_2ddbu ligand, centered on the ruthenium atom, also shows an increased amplitude (Fig. 5(D)). The flexibility of the Me_2ddbu ligand is crucial here, allowing the ruthenium coordination sphere to rearrange thus accommodating the electronic and steric changes taking place upon water binding.

The final key difference between C1 and C2 is observed in the time dependent behavior of the dbcot ligand. Upon water coordination, the angle between the rings initially increases within the first 700 fs, then it sharply decreases back to its initial value (Fig. 5(E)). Similar to the C1 catalyst, the dbcot ligand is attracted toward the metal center while the H_2

molecule remains in the proximity to the ruthenium atom. However, upon the coordination of a water molecule and subsequent displacement of H_2 , the ligand relaxes and reverts to its initial geometry. This dynamic behavior is further corroborated by a corresponding variation in the distance between two carbon atoms, one from each opposing ring (Fig. 5(F)).

DRC trajectory for complex C3 reveals a distinct behaviour compared to C1 and C2. In this case, although H_2 is formed, it fails to escape the complex (Fig. 6(A)). Instead, as evidenced by the oscillations commencing around 700 fs, the dihydrogen molecule remains adsorbed on the ruthenium surface. Concurrently, the distance between the two hydrogen atoms significantly increases beyond the typical H–H bond length (0.74 Å), indicating its dissociation into two hydrogen atoms that are free to diffuse across the ruthenium surface (Fig. 6(B)).

Furthermore, the water molecule, which typically facilitates dihydrogen displacement from the ruthenium surface, does not approach the metal center in C3. Instead, it remains at a considerable distance of approximately 3 to 4 Å from both the ruthenium and the phosphorus atoms (Fig. 6(C) and (D)).

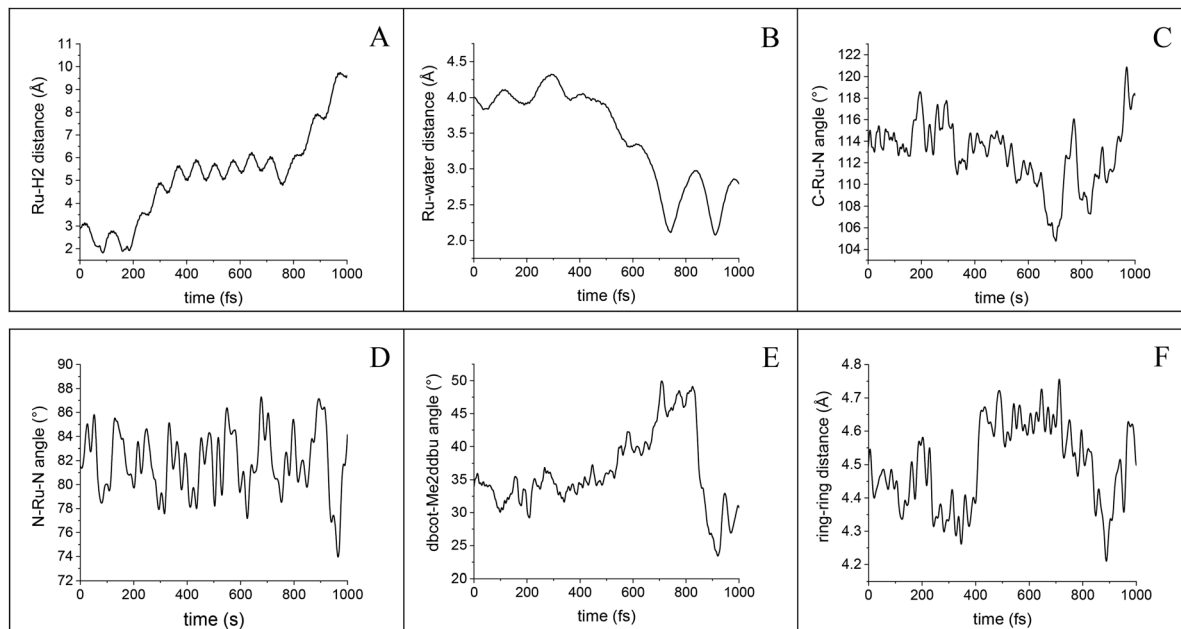


Fig. 5 C2 catalyst intermolecular geometrical parameters as a function of time, DRC calculation performed with 5 kcal mol⁻¹ total kinetic energy. Results obtained at 10 kcal mol⁻¹ are shown in Fig. S2. (A) distance of the H atom dissociating from Ru. (B) water molecule, Ru distance. (C) variation in the angle between the dbcot C atom and the Me₂ddbu N atom centered on Ru. The C and N atoms are *cis* to Ru. (D) N–Ru–N angle. (E) variation in the angle between dbcot benzyl ring and Me₂ddbu plane. (F) variation in the distance between the two dbcot benzyl rings.

We initially hypothesized that steric hindrance imposed by the three bulky quinoline ligands prevented water from approaching the core of the complex. To investigate this, we analyzed the relative motions between the ligands. The DRC trajectory revealed that only one of the three Qn ligands exhibits significant motion, while the other two maintain their positions relative to each other and the P–Ru axis. This finding led us to focus our analysis exclusively on the dynamics of this single mobile ligand.

By examining the distance between this moving ligand and the water molecule, we noted that the ligand–water distance increases while the water–ruthenium distance remains constant. This implies that the ligand moves away from the water molecule, rather than obstructing the motion of H₂O towards the Ru center. Therefore, we ruled out steric repulsion as the primary cause for the remote position of water (Fig. 6(E)). This “opening” motion of the ligand relative to the Ru–water axis is further corroborated by the variation in the angle between the moving ligand and the two stationary Qn ligands, considered individually (Fig. 6(F) and (F)). Lastly, observing the distance between the ruthenium atom and the nitrogen atom of the moving Qn ligand (Fig. 6(H)) reveals only a slight increase in bond vibration over time. This suggests that the motion of the ligand is primarily rotational around the Ru–P axis, rather than translational.

To investigate whether C3 inability to release H₂ could be overcome by additional kinetic energy, we performed DRC calculations at 10 and 25 kcal mol⁻¹. These energies were specifically selected to exceed its activation energy barrier (5 kcal mol⁻¹ higher than complex C1 and 16 kcal mol⁻¹ higher

than complex C2). Nevertheless, hydrogen remained persistently bound to the ruthenium surface even under these high energy conditions.

4.3 Transition state electronic properties

Sections 4.1 and 4.2 show that both steady-state and time-dependent results are characterized by a marked difference in the catalytic activity of the three ruthenium complexes considered. Specifically, C3 keeps the molecular hydrogen trapped within its coordination sphere, while C1 and C2 lead to the effective release of H₂, as experimentally observed for the C1 complex.³⁸ Therefore, it is crucial to pinpoint and understand how the role of electronic molecular properties of these complexes govern the observed differences in their chemical reactivity. The analysis of the HOMO and LUMO spatial distribution is often employed for such a purpose.^{47–50}

Fig. 7 shows the LUMO distribution of the transition states of the three complexes. A striking qualitative difference is found in the LUMO: the LUMO of the C1 and C2 complexes extends significantly towards the region of H₂, while the LUMO of the H₂ molecule exhibits bonding character between its two hydrogen atoms and an anti-bonding interaction with respect to the ruthenium atom. Interestingly this is not the case for C3: its LUMO does not show any significant presence on the H₂ molecule. Indeed, the third-highest unoccupied MO shows a lobe localized on the H₂ molecule (compare with Fig. S6), but the energy of such an unoccupied MO is lying 0.8 eV above the LUMO energy.

The occupied and virtual orbital energies, along with the HOMO distribution for catalysts C1, C2, and C3, are provided in

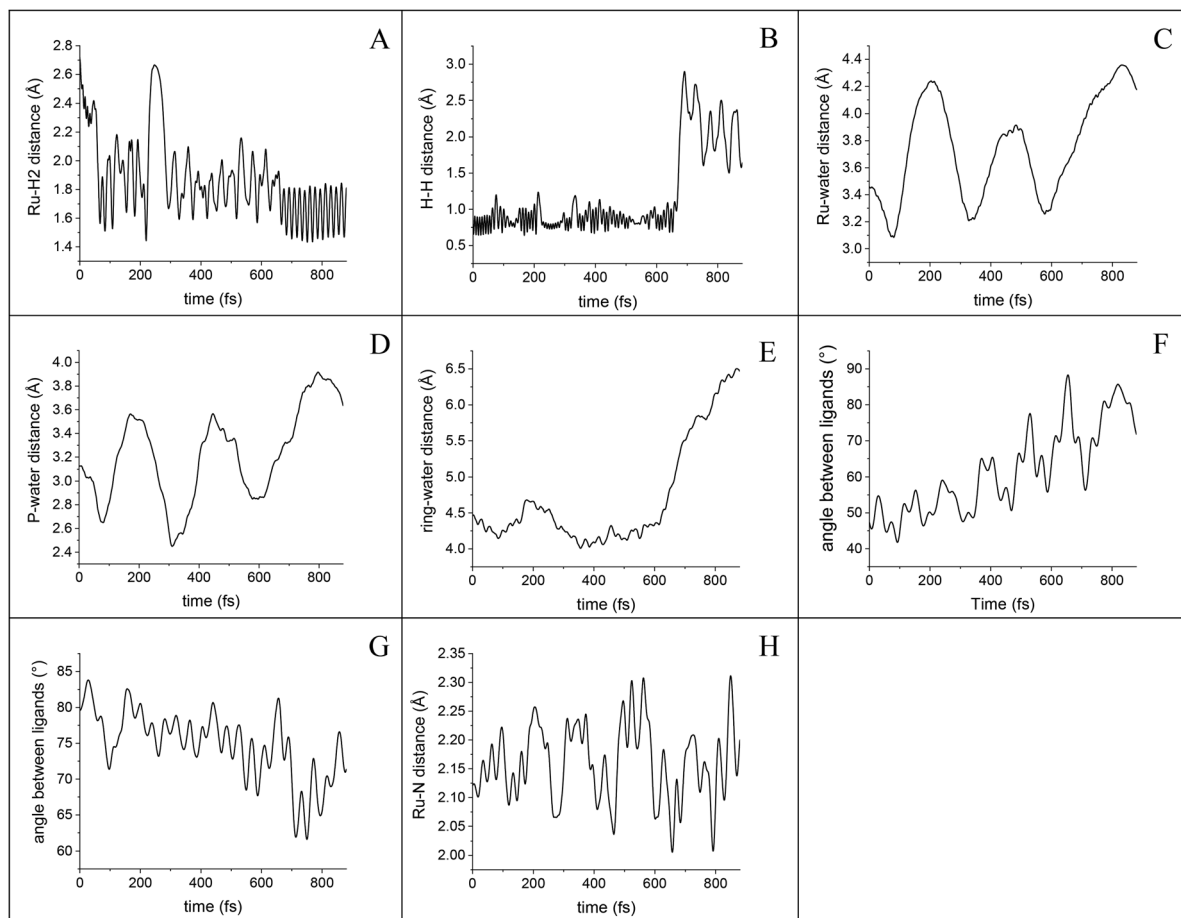


Fig. 6 C3 catalyst intermolecular geometrical parameters as a function of time, DRC calculation performed with 5 kcal mol^{-1} total kinetic energy. Results obtained at 10 kcal mol^{-1} and 25 kcal mol^{-1} are shown in Fig. S3 and S4 respectively. (A) distance of the H atom from Ru. (B) H–H distance. (C) water molecule, Ru distance. (D) water molecule, P atom distance. (E) water molecule, Qn ring distance. (F) and (G) variation in the angle between two Qn ligands. Only two pairs are shown, the angle between the third pair changes only slightly. (H) variation in the distance between a N atom of Qn and Ru.

(Section 3 and Fig. S6). The HOMO of each complex share a common feature: the HOMO is not localized on the hydrogen molecule (see Fig. S7). This suggests that the reactivity of this class of Ru-based catalysts toward hydrogen is not driven by the HOMO, but rather by the anti-bonding character of the LUMO, which is localized between the ruthenium atoms and the H_2 molecule. The lack of HOMO localization on H_2 provides a strong rationale for the effectiveness of these compounds in hydrogen production.

5. Conclusions

This study elucidates the role of electronic properties in governing the hydrogen evolution reaction (HER) of mono- and dinuclear ruthenium-based catalysts. Using a combination of DFT calculations to characterize steady-state behavior and MD simulations *via* the DRC algorithm, we have provided a detailed, atomic-level understanding of the catalytic mechanism. Our computational results align with the previously proposed multi-step HER mechanism for the C1 $[\text{Ru}_2(\mu\text{-H})(\text{Me}_2\text{dad})(\text{dbcot})_2]$ complex by Vizza and co-workers,³⁸ offering

new insights into the role of water in the rate-determining step: the dihydrogen displacement from the active site.

Our comparative analysis highlights the crucial impact of subtle structural differences on catalytic efficiency. While the C2 catalyst shows a remarkably low activation barrier ($8.6 \text{ kcal mol}^{-1}$, compared to $19.5 \text{ kcal mol}^{-1}$ for C1 and $24.4 \text{ kcal mol}^{-1}$ for C3), its product release is kinetically slow. In contrast, the most significant finding from this study is the behavior of the C3 catalyst. Despite having favorable energetics and successfully forming an H_2 molecule, the complex completely fails to release the product. Instead, the H_2 molecule dissociates into individual hydrogen atoms that remain bound to the ruthenium atom. This revealed an unforeseen kinetic barrier and underscores that factors beyond simple activation energy, such as ligand coordination flexibility and the ability of solvent molecules to approach the active site, are paramount for effective catalysis.

Analysis of molecular orbital distributions confirmed that the differences in catalytic activity are governed by the spatial distribution of the LUMOs. For the active C1 and C2 complexes the LUMO extends on the H_2 molecule, having anti-bonding

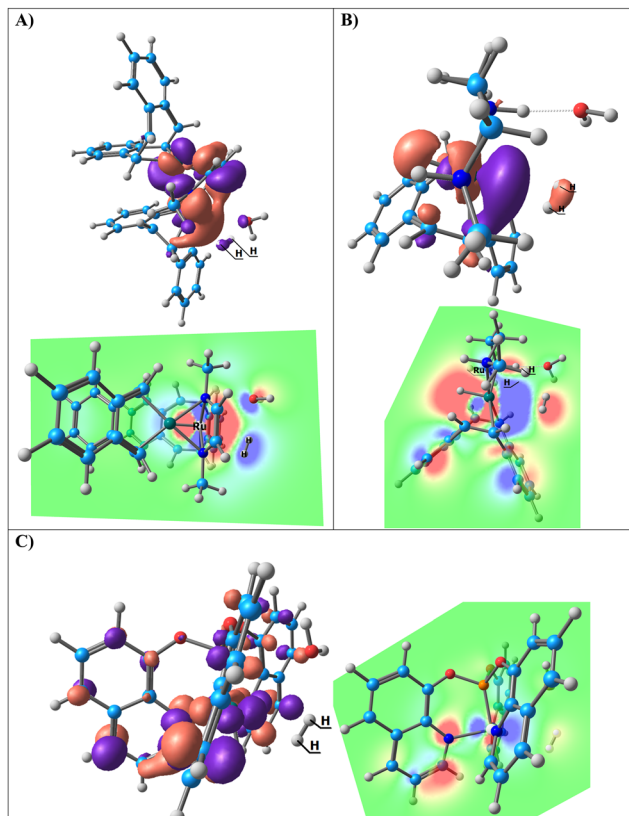


Fig. 7 Transition state LUMO 3D virtual electron density distribution of the three Ru based catalysts. PBE0-D3BJ/def2-SVP/def2-TZVP(Ru) level of the theory, together with their relevant 2D projection on the plane containing the hydrogen molecule and the closest ruthenium atom. (A) C1 (B) C2 (C) C3.

character between the ruthenium atom and the H_2 molecule. This electronic feature is critical for facilitating hydrogen release. In contrast, the ineffective C3 complex shows a stark difference: its LUMO lacks any significant presence on the H_2 molecule and the relevant orbital for H_2 release is located at a much higher energy level, rendering the release pathway kinetically inaccessible. This key finding underscores that the electronic properties of the LUMO, and not just activation energy barriers, are the determining factor for product release.

This work provides a rule-of-thumb for the rational design of next-generation HER catalysts. By identifying that dynamic behaviour and the presence of kinetic traps can undermine promising energetic profiles, and the role of anti-bonding molecular orbitals, our findings offer a new paradigm for catalyst development. This allows for the strategic rejection of designs (such as the motif in C3) that may appear favourable from a steady-state perspective but are ultimately ineffective. Future work will explore other ligand modifications to optimize both activation energy barriers and favourable product release dynamics.

Conflicts of interest

The authors declare no conflicts of interest.

Data availability

The data supporting this article and details concerning the calculations (basis-set cross-check, DRC additional trajectories at higher initial kinetic energy, transition states electronic properties, some example of input files) have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5cp03035h>.

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