

Hydrogen transfer reaction to imines with 2-propanol catalyzed by ruthenium (II) complexes containing nitrogen-phosphorus (NPN) ligands. Experimental and computational studies

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A B S T R A C T

This work reports the synthesis and characterization of ruthenium(II) complexes containing nitrogen-phosphorus-nitrogen (NPN) ligands, with L1 = N-(phenyl (pyridin-2-ylamino)phosphino)pyridin-2-amine and L2 = 4-methyl-N-((4-methylpyridin-2-ylamino)(phenyl)phosphino)pyridin-2-amine. The ruthenium complexes RuCl₂PPh₃(L1) (1) and RuCl₂PPh₃(L2) (2) show high activities in catalytic transfer hydrogenation of different substituted benzylideneanilines, with turnover frequencies up to 5882 h⁻¹ and 5294 h⁻¹, respectively. The RuCl(CO)PPh₃(L1) (3) and RuCl(CO)PPh₃(L2) (4) complexes were non-active in the reaction studied. Theoretical calculations conducted for complex 4 showed that the carbonyl group promotes σ-orbital interactions and backdonation phenomena from the metal centre to the π* orbitals in the CO ligand, presenting a strong orbital contribution. This supports the hypothesis that complexes 3 and 4 are less reactive species and therefore present poor or null catalytic performance in the reaction studied.

1. Introduction

Amines are key building blocks in the preparation of many pharmaceutically important products, among which are included stimulants, vasoconstrictors, decongestants, anti-histamines, and anti-depressants; its use in medicine dates back at least a century [1,2]. The catalytic imine hydrogenation is in many cases the best way to cleanly prepare them. This is especially useful when the synthetic goal is the preparation of chiral amines. Catalytic transfer hydrogenations (TH) have several advantages over the use of molecular hydrogen, such as simple operation (does not require pressurized gas and special equipment), and in general, requires inexpensive and readily available hydrogen donors. The catalytic transfer hydrogenation of imines using 2-propanol/base as a hydrogen source with transition metal complexes derived from different ions, such as Ru (II), Rh (I), Ir (III), and Ni (0), has been widely used [3–8]. Additionally, palladium compounds have been also used for the reduction of different organic substrates using homogeneous and

heterogeneous conditions [9–14]. Ruthenium(II) complexes containing phosphorus-nitrogen (PN) ligands proved to be very robust catalysts for various catalytic hydrogenation reactions [15–17]. Additionally, ruthenium hydroxycyclopentadienyl complexes exhibit moderate activities in the hydrogen transfer reaction to imines, where the mechanism suggests that the imine coordinates to the metal in the first step before the hydrogen transfer reaction occurs [18]. Ruthenacycle complexes have been also used in the TH of several substituted N-benzylideneanilines showing good functional group tolerance with TOFs up to 12 h⁻¹ [19,20]. Recently, a ruthenium complex containing an aliphatic PNP ligand, well known for its excellent performance in the dehydrogenation of methanol [21,22], was found to be an effective catalyst for the transfer hydrogenation of several imines using a MeOH/NaOMe reduction system, reaching TOFs up to 4.2 h⁻¹. Non-noble transition metals are also found to be efficient catalysts for the TH reaction. For instance, the reduction of quinolines and imines catalysed by simple manganese carbonyl compounds (Mn₂(CO)₁₀ or MnBr(CO)₅) has been

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described. The non-noble complexes exhibited conversions between 34 % and 100 % using molecular hydrogen as the reducing agent [23]. Also, nickel complexes were found to be active catalysts in the hydrogenation of *N*-*t*Bu-sulfonyl imines. The reaction was performed using a high substrate/catalyst ratio resulting in conversions between 96 % to 98 %; however, it requires a longer reaction time [24,25]. Our group has successfully developed catalytic applications in hydrogen transfer reactions to imines using ruthenium(II) as well as palladium(II) compounds with PN ligands [26–30]. We recently reported on the synthesis and characterization of nickel(II) complexes that contain PN ligands. These complexes were designed for the reduction of *N*-benzylideneaniline, using formic acid as a reducing agent. The complexes exhibited high catalytic activity under mild conditions, exhibiting the versatility of the bidentate PN ligands with various metal centres [31]. It has been widely demonstrated that the ancillary ligand in metal complexes plays a crucial role in tuning the efficiency and selectivity of the catalytic reaction. For instance, the phosphorus atom could stabilize the metal centre in lower oxidation states by its π -acceptor nature, while the σ -donor feature of the nitrogen could stabilize higher oxidation states [32]. The presence of these ligands provides the metal centre versatility in the coordination number or intermediate geometries during the catalytic reaction and, in turn, allows the coordination of the substrate as well as the dissociation of the product at the end of the catalytic cycle [33]. In previous research, we conducted theoretical calculations for a ruthenium(II) complex containing a PN ligand and carbonyl groups (*trans*-Cl-*cis*-(CO)-[Ru(CO)₂Cl₂(PN)] (where PN = diphenylphosphine-aminopyridine), to rationalize its catalytic properties and the role of the ancillary ligands [34]. In this work, it was demonstrated that the orbital contribution of the PN ligand stabilized the metal centre, allowing an efficient catalytic performance. In previous work, we have introduced the TH of *N*-benzylideneaniline using the complexes RuCl₂PPh₃(L1) (1) and RuCl₂PPh₃(L2) (2) as catalysts (see molecular structures of ligands L1 and L2 in scheme 1 [35]). Here we complement this previous research by expanding the substrate scope of the catalysts. Complexes 1 and 2 were also active catalysts in the hydrogen transfer reaction of other substituted imines, with conversions ranging from 23 % and 95 % at different reaction times. Additionally, theoretical studies were conducted to get insight into the reactivity of complexes RuCl(CO)PPh₃(L1) (3) and RuCl(CO)PPh₃(L2) (4) that exhibit null catalytic activity, despite having similar ligands and structures than compounds 1 and 2. These studies also support the discussion on the complexes reactivity including the potential intermediates formed during the catalytic process.

2. Experimental

2.1. General considerations

The substrates and reagents were purchased from Aldrich or Merck and purified using the methods described in the literature [36]. All reactions were carried out under an N₂ atmosphere (Schlenk tube). FT-IR spectra were recorded on a Bruker IFS-28 V FT-IR spectrophotometer. Elemental analysis was carried out using a Thermo Scientific Flash 2000 model while ¹H NMR and ³¹P{¹H}-NMR spectra were recorded on a

Bruker Avance DRX 400 MHz spectrometer. The ligands and complexes were synthesized using methods described by our laboratory in previous works [35] (see [supplementary material](#)).

2.2. Structural determination

The crystal structures of complexes 1 and 4 were determined by X-ray diffraction at 298 K, using a Bruker SMART-APEX II CCD diffractometer system [37,38]. Table 1S-4S, Fig. 1S (see [supplementary material](#)) [39] shows a summary of structural and refinement details.

2.3. Catalytic transfer hydrogenation experiments

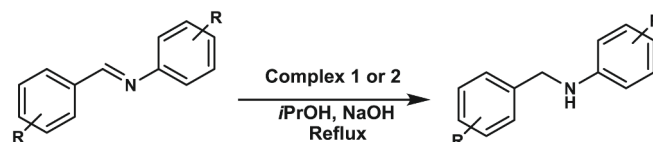
The catalyst (0.01 mmol) was dissolved in 2-propanol (8 mL), and the solution was refluxed for 10 min then the imine substrate (10 mmol) was added, and the mixture was refluxed for another 5 min. The catalytic reaction was initiated by the addition of sodium hydroxide (9.9 mg, 0.24 mmol) dissolved in 2-propanol (1 mL). The reaction progress was monitored by gas chromatography with periodic sampling. Gas chromatographic analysis was carried out with a Hewlett-Packard Agilent 5890 N chromatograph instrument equipped with FID, using an Equity-1 column and N₂ as the carrier gas. GC-mass spectra were run to confirm the identity of products on a MAT 95 XP Thermo Electron (scheme 2).

2.4. Computational details

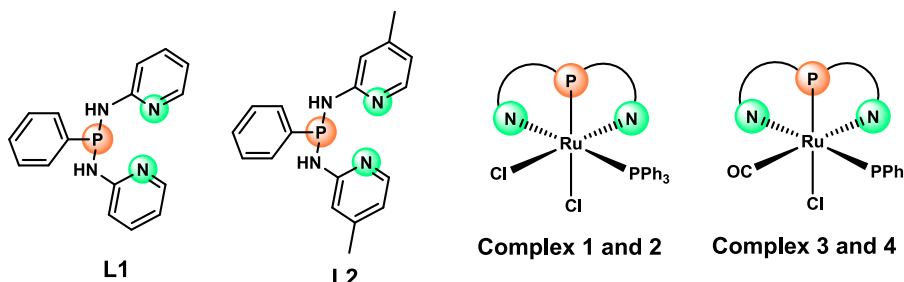
2.4.1. Density functional theory calculations

Density functional theory (DFT) calculations were used to study the molecules involved in this work (complex 1 and complex 4). These complexes were drawn using Discovery Studio Modelling Environment 3.1 [40]. Geometries were optimized using the GGA functional BP86 [41] composed of the Becke 1988 exchange functional and the Perdew 86 correlation functional, and 6-311++G(d,p) basic set [42] was used for the atomic description of Cl, P, N, C, O and H atoms, whereas the LANL2DZ pseudopotential [43] was adopted for ruthenium transition metal. All calculations were carried out using the Gaussian16 program [44]. The Electron Localization Function (ELF) was performed using MultiWFN software for wavefunction analysis [45]. When the ELF value is high, it suggests that there is a strong concentration of electrons in a specific area, which would indicate the presence of a covalent bond, lone pair, or the involvement of inner shells of the atom. The ELF is a useful tool for studying various systems, including small organic and inorganic molecules, as well as coordination compounds.

To evaluate the molecular electrostatic potential (MEP) of the Ru (II)



Scheme 2. Hydrogen transfer to imine using 2-propanol as hydrogen source.



Scheme 1. Molecular structures of ligands L1 and L2 and complexes 1 to 4.

complexes, a calculation of their electron density and electrostatic potential was performed in the first place, using the cubegen tool of the Gaussian16 computational package [44]. To gain a better understanding of a molecule's reactivity, certain global reactivity descriptors based on DFT (Density functional theory), and following Koopmans' theorem were computed (as listed in Table 1). These descriptors include HOMO-LUMO gap, electronegativity (χ), global hardness (η), global electrophilicity index (ω), ionization potential (I), and electron affinity (A).

3. Results and discussion

3.1. Structural description

The crystal structure of complexes **1** and **4** (Fig. 1S, Supplementary material) shows the main distances and angles of the related compounds. The crystal structure of complex **1** shows two remarkably similar but non-equivalent molecules of the compound [35]. The coordination environment around the ruthenium (II) centre in each complex would be well described as a non-regular and slightly distorted octahedron with the NPN atoms from **L1** or **L2** respectively occupying facial positions, two chlorides (complex **1**) or one chloride, and a carbonyl (complex **4**), with triphenylphosphine in the remaining one. The crystal data, selected bond distances and selected angles are summarized in the supplementary material (tables 1S, 2S, 3S, 4S, and 5S). To the best of our knowledge, there is just one similar complex previously described, (PPh(NHPy)₂W(CO)₃ [57].

3.2. Catalytic results

The catalysts RuCl₂PPh₃(L1) (**1**) and RuCl₂PPh₃(L2) (**2**) achieved high conversions in the transfer hydrogenation of *N*-benzylideneaniline and other substituted imines, however, complexes RuCl(CO)PPh₃(L1) (**3**) and RuCl(CO)PPh₃(L2) (**4**) were not active in the hydrogen transfer to imines with 2-propanol/NaOH as reducing system. To expand the substrate scope, we took complexes **1** and **2** to assess their catalytic performance with different imines as shown in Table 2. In general, the results indicated high conversions and selectivity with TOFs around 5882–113 h⁻¹. The maximum conversion depends on the nature of the imine and was variable with the reaction time. Interestingly, most of the substrates were fully hydrogenated after the appropriate reaction time. The selectivity towards the secondary amine was 100 % for all the substrates, demonstrating the great performance of complexes **1** and **2**. The reported high activities of the ruthenium catalysts obtained in this work allow us to confirm that synthetic design mixing both electronic and geometrical properties are key features for obtaining highly active and selective catalysts. According to the crystal structure of complex **1**, the *cis*-chlorine and *cis*-phosphorus configuration was confirmed. To get

insight into the mechanism of the catalytic reaction, it is essential to know the structure of the complexes. In this regard, complex **1** has an octahedral configuration with two *cis*-chlorine and one triphenylphosphine. These three ligands are in a *facial* configuration around the metal centre. We hypothesize that this specific arrangement may facilitate the creation of a ruthenium dihydride compound. This could be followed by the removal of a phosphine ligand, resulting in a vacancy that allows the substrate to coordinate with the catalyst and promote the desired chemical reaction. The catalytic results obtained could be explained using an inner-sphere or outer-sphere mechanism. We performed several experiments to determine if the –NH– group (potentially Brønsted acidic) assists the formation of the ruthenium hydride or the subsequent formation of the amine, not finding experimental evidence to confirm this hypothesis. The result obtained suggests an inner-sphere mechanism, since when a Cl ligand was replaced for CO the activity of the catalyst is null. This is in agreement with the theoretical study, since the CO group is a less labile ligand. In a previous research [35], we were able to identify a ruthenium hydride intermediate using ¹H NMR, indicated by a multiplet at –18 ppm. This helped us to understand why the different substrates exhibited high activities and selectivity when the substrate/catalyst ratio was 1000/1. The catalytic results achieved in this study were superior to those previously reported using ruthenium complexes containing polypyridine ligands [28]. On the other hand, complexes **3** and **4** were not active catalysts in the hydrogen transfer to *N*-benzylideneaniline using 2-propanol. If we analyse the inner-sphere catalytic hydrogen transfer reaction mechanism previously reported [58], three coordination sites are required for an effective catalytic process. Two of them are required to form a metal dihydride and a third site is needed to coordinate the substrate to the metal centre. We suggest that the difference in reactivity of these complexes relies on the coordination fashion presented in their structure, as well as the nature of the ancillary ligands. The structural coordination of complexes **1** and **2** shows two chlorines and one phosphine in the *facial* configuration. The chlorines facilitate the creation of a metal dihydride (partially confirmed by ¹H NMR), and the phosphine acts as a labile ligand that generates a coordinating vacancy, allowing the substrate to bond to the metal centre. Although complex **3** and complex **4** have a *facial* configuration, formed by one chlorine, a carbonyl, and a triphenylphosphine ligand, we suggest that they indeed form a hydride species. However, the carbonyl group, unlike phosphine ligands, is not labile enough and remains coordinated to the metal centre, inhibiting the generation of the coordinating site necessary for the catalytic process. Thus, the poor reactivity of complex **3** and complex **4** seems to be related to the low lability of the carbonyl group which also could stabilize low oxidation states of ruthenium, making the catalytic species less reactive.

The results summarized in Table 2 confirm that the dichloride complexes **1** and **2** are active in the transfer hydrogenation of substituted imines, obtaining the secondary amine as the major product. When the phenyl rings of the imine substrate are substituted in the –*para* position with electron-withdrawing groups (entries 3 and 4), the reaction rate decreases, requiring up to 4 h to achieve conversions close to 100 %. Meanwhile, the decrease in activity is less pronounced when substituents such as –OMe are introduced into the aromatic ring of the substrate (entry 2). Nevertheless, it is not conclusive that the change in the reaction rates is only affected by the electronic properties of the substrate. Substituents into the aromatic ring of the substrate may hinder its approximation (coordination) to the active centre of the catalyst. Thus, we also suggest that the steric effect might play an important role in this catalytic system.

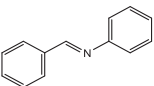
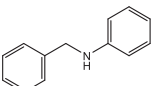
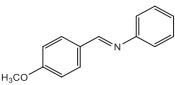
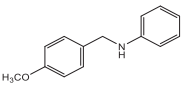
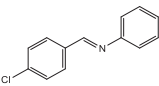
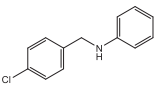
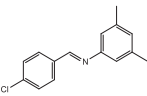
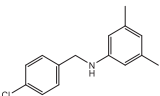
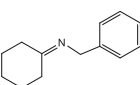
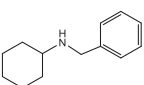
After comparing the reported activities of complexes **1** and **2** with those in the literature, it was found that they exhibit higher conversions in shorter reaction times than previously reported [23,31]. For example, *N*-benzylideneaniline is selectively hydrogenated in only 10 min of reaction and the presence of imine hydrolysis is not observed. On the other hand, nickel (II) complexes also catalyse this reaction, though the reaction requires up to six times more reaction time to achieve similar

Table 1
Equations for global and local reactivity indexes calculated in the TAFF [46] pipeline.

	Koopmans' theorem	Reference
Electronegativity (χ)	$\chi = -\frac{1}{2}(\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}})$	[47–49]
Electrophilicity (ω)	$\omega = \frac{\mu^2}{2\eta} = \frac{(\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}})^2}{2(\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})}$	[50]
Ionization potential (I)	$I = -\epsilon_{\text{HOMO}}$	[51]
Electron Donator (A)	$A = -\epsilon_{\text{LUMO}}$	[51]
Global Hardness (η)	$\eta = \frac{1}{2}(\epsilon_{\text{L}} - \epsilon_{\text{H}})$	[47,52–56]
HOMO-LUMO Gap (ΔE)	$\Delta E = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$	[51]

* ϵ_{LUMO} = Lowest Unoccupied Molecular Orbital energy and ϵ_{HOMO} = Highest Occupied Molecular Orbital energy.

Table 2
Hydrogen transfer to imines, catalysed by complexes **1** and **2**.

Entry	Substrate	Product	Complex 1 (% Yield (time), TOF h ⁻¹)	Complex 2 (% Yield (time), TOF h ⁻¹)
1			90(0.17 h), 5294	95(0.17 h), 5882
2			99(1 h), 999	100(1 h), 1000
3			17(1 h), 170 60(2 h), 300 90(4 h), 225	23(1 h), 230 34(3 h), 11367 (4 h), 168
4			27(2 h), 135 40(3 h), 225 80(4 h), 200	32(2 h), 16042 (3 h), 140
5			63(2 h), 315 98(3 h), 327	70(2 h), 35099 (3 h), 334
6			25(2 h), 125 34(3 h), 114	35(2 h), 17543 (3 h), 144

Conditions: substrate/NaOH = 1/10; substrate/catalyst = 1000/1; T = 80 °C. Isolate Yield; N-benzylaniline (85 %); N-(4-methoxybenzyl)aniline (80 %); N-(4-chlorobenzyl)aniline (90 %); N-methyl-1-phenylmethanamine (87 %).

conversion [31]. Complexes **3** and **4** were not active in the hydrogen transfer reaction of imines. These complexes contain a carbonyl ligand in their structure, which stabilizes the complex, preventing it from reacting with 2-propanol to form the Ru-H species, due to the π back-bonding effect of the carbonyl as mentioned above. The computational studies presented later in this work suggest that the carbonyl group promote σ -orbital interactions and backdonation phenomena from ruthenium (II) to the π^* orbitals in the CO ligand, which could explain the null activity of these complexes in the transfer hydrogenation of imines.

The two complexes studied as catalysts (**1** and **2**) in the TH of substituted *N*-benzylideneanilines showed superior activity to other ruthenium (II) and nickel (II) complexes studied for the same reaction as shown in Table 3. All previous reported in transfer hydrogenation of *N*-benzylideneaniline request a longer reaction time and the amounts of substrate are lower than those reported by us.

4. Molecular and electronic structure

The computational calculations were done at the BP86/TZ2P level of theory. The most important geometrical details are listed in Table 4. The

Table 3
Comparison of the catalytic transfer hydrogenation of *N*-benzylideneaniline between complex **2** and other Ru-based and Ni-based catalysts reported in the literature.

Catalyst	T (°C)	Time (h)	S/C	Reducing system	TOF (h ⁻¹)	Reference
Complex 2	82	0.17	1000	<i>i</i> PrOH/NaOH	5882	This work
Ru(PNP)	120	12	50	MeOH/NaOMe	4.1	[22]
Ru(II)–NHC	82	24	50	<i>i</i> PrOH/KOH	12	[19]
Ru(PN)	82	3	200	<i>i</i> PrOH/NaOH	64	[34]
Ni(PN)	80	3	400	CH ₃ CN/HCOOH	128	[31]
Ru(NN)	82	6	200	<i>i</i> PrOH/NaOH	30	[29]

bond lengths around the ruthenium (II) metal centre, chlorine, and CO ligand are consistent with the experimental X-ray single crystal data. Additionally, the bond distances for Ru(II)–Cl, Ru(II)–CO, Ru(II)–P, and Ru(II)–N are in agreement with other similar crystallographic structures [46,59,60] (see Table 4). The frontier orbitals of Ru(II) complexes obtained with BP86/TZ2P are depicted in Fig. 2. The results represent both the highest-occupied molecular orbitals (HOMOs) and the lowest-unoccupied molecular orbitals (LUMOs). For complex **1** the main contributions in the HOMO orbital are from d orbitals associated with the metal centre and p orbitals associated with the chlorine ligand. In contrast, the LUMO has d orbitals contributions from the Ru(II) and p orbitals located in the NPN ligand. In the case of complex **4**, a similar situation occurs, with the difference that the triphenylphosphine ligand (p orbitals) has an important participation in the distribution of the electronic density. A comparison between the ideal octahedron and the geometric parameters obtained for the ruthenium (II) complex shows a slight deviation, due to adjacent CO, chlorines, and NPN ligand (equatorial) which present angles less than 90°.

5. Bonding properties and reactivity

To support and enlarge the reactivity discussion previously done, an analysis of the bonding energetics was performed. In agreement with the Morokuma–Ziegler (EDA) scheme [61], combinations of a fragment approach to the molecular structure with the decomposition of the interaction energy between fragments can be decomposed as shown in equation (1).

$$E_{int} = \Delta E_{Pauli} + \Delta E_{elstat} + \Delta E_{orb} \quad (1)$$

Where ΔE_{Pauli} , ΔE_{elstat} , and ΔE_{orb} are the Pauli repulsion, electrostatic interaction, and orbital-mixing terms, respectively.

In this framework, a combination of the extended transition state theory and the natural orbitals for chemical valence (ETS-NOCV) [62–64] analysis along with the Morokuma–Ziegler scheme was done to analyse the orbital contributions to the bonding properties in the ligand–metal interactions. Table 5 shows the different quantities

Table 4

Bond distances calculated for complexes **1** and **4** at the BP86/LANL2DZ/6–311++G(d, p) level of theory. Distances are given in Å. (experimental bond distances see supplementary material).

Complex	d CO	d Ru(II)-Cl(1)	d Ru(II)-Cl(2)	d Ru(II)-N(1)	d Ru(II)-N(2)	d Ru(II)-P(1)	d Ru(II)-P(2)	d Ru(II)-C
1	—	2.466	2.424	2.117	2.173	2.153	2.328	—
4	1.160	2.475	—	2.215	2.184	2.184	2.344	1.833

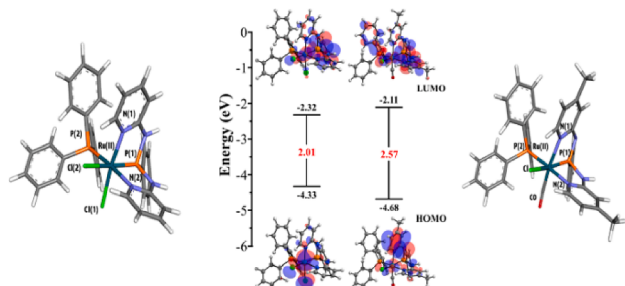


Fig. 2. Relativistic DFT optimized geometry of complex **1** and **4**, with a graphical representation of the frontier orbitals (HOMO and LUMO) (BP86/TZ2P).

involved in the Morokuma Energy decomposition analysis. The molecule with the carbonyl ligand (complex **4**) showed high orbital contributions (46 %) compared to the chlorine ligand located in the same coordination position (this shows the greater lability that the chlorine ligand presented in complex **1**). Therefore, it allows the formation of metal di-hydride in a *facial* configuration. In contrast, complex **4** did not show catalytic activity in the imine hydrogenation reaction explained by the higher orbital contribution. Additionally, the carbonyl group promotes σ -orbital interactions and backdonation phenomena from Ru(II) to the π^* orbitals in the CO ligand. This ensures a strong orbital contribution.

To enhance the previous analysis, the reactivity and sites that are susceptible to nucleophilic, electrophilic, or radical attack of the isolated complexes were determined using the corresponding Fukui function. This calculation revealed the increased reactivity of the molecules being studied, and the positions of the lobes indicated the most probable sites for the corresponding attack. The electron densities on the isosurfaces displayed in Fig. 3 revealed the involvement of the metal *d* orbitals, indicating an active charge transfer process.

The regions for f^- , f^+ , and f^0 , also indicate that the most probable sites where an electrophilic, nucleophilic, and radical attack may occur are through Cl⁻ and NPN ligands, whereas the nucleophilic attack can also occur in the triphenylphosphine ligand. The CO ligand does not participate in any of the reactivity schemes used. This reinforces the evidence that molecule **4** does not exert catalytic activity. Additionally, it has been shown that complexes with an architecture of molecule **1** generate a vacant site, and then undergo heterolytic splitting to give the ruthenium hydride. The computational results show that a protic environment favours the formation of this species. Following Koopmans' theorem, we calculated the following global reactivity descriptors shown in Table 6. Electrophilicity (ω) values showed that complexes **1** and **4** have values greater than 1.50 eV. Compound **1** exhibits a larger value than complex **4**. This characterizes it as a stronger electrophile.

Table 5

Analysis of the Morokuma Energy decomposition. All values are given in kcal/mol.

Fragment	ΔE_{Pauli}	ΔE_{elec}	ΔE_{orb}	BE	%Elstat	%Eorb
Cl-RuClPPH ₃ (L1)	103.19	-143.84	-77.59	-123.72	65	35
CO-RuClPPH ₃ (L2)	223.41	-155.19	-132.08	-68.96	54	46

6. Conclusions

From the experimental and computational results, we can conclude that complexes of ruthenium (II) containing chlorines, triphenylphosphine, an NPN-ligand and/or carbonyl were obtained. The structural characterization and theoretical evidence indicate distorted octahedral geometries for complexes **1** and **4**. Complex **1** shows two *cis*-chlorines with *cis*-phosphorus; these three ligands are in facial configuration around the metal centre. Complex **4** has a facial configuration, formed by one chlorine, a carbonyl, and a triphenylphosphine ligand. From catalytic studies, it is possible to conclude that complex **1** and complex **2** are highly active catalysts, reaching around 100 % conversion for the reduction of imines, while complex **3** and complex **4** are not active in such a reaction. It is suggested that the carbonyl group, unlike phosphine ligands, is not labile enough and remains coordinated to the metal centre, inhibiting the generation of the coordinating vacancy needed for the catalytic process. The theoretical studies for complex **4** showed high orbital contributions from the carbonyl group, supporting the hypothesis of a less reactive species and therefore poor catalytic performance. The Fukui functions display the main regions for an electrophilic (base) or nucleophilic (acid) attack on the molecules under study indicating that the most probable sites where an electrophilic, nucleophilic, and radical attack may occur are through Cl⁻ and NPN ligands, whereas the nucleophilic attack can also occur in the triphenylphosphine ligand. The CO ligand does not participate in any of the reactivity schemes used, reinforcing the evidence that compound **4** does not exert catalytic activity. Additionally, the good performances on the hydrogenation of different imines confirm the potential of these systems to be used in other catalytic reactions.

CCRediT authorship contribution statement

Camila Negrete-Vergara: Validation, Formal analysis, Data curation. **Andrés Vega:** Validation, Formal analysis. **Plinio Cantero-López:** Writing – original draft, Software, Formal analysis. **Osvaldo Yáñez:** Software, Formal analysis. **Sergio A. Moya:** Writing – original draft, Resources, Conceptualization. **Gonzalo Valdebenito:** Visualization,

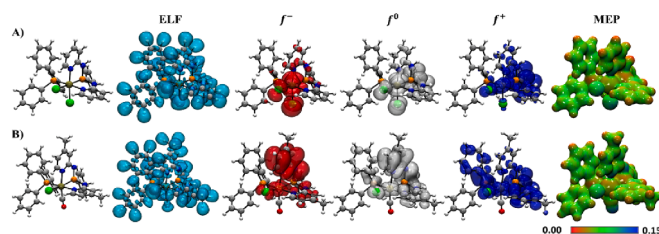


Fig. 3. Graphical representation of the electron localization function (0.8 a.u.), electrophilic f^- , radical f^0 , and nucleophilic f^+ Fukui functions (0.0005 a.u.), and electrostatic potential maps (0.2 a.u.) of A) Complex **1** y B) Complex **4** at the BP86/LANL2DZ/6–311++G(d, p) level of theory.

Table 6

Frontier molecular orbital and global reactivity indexes obtained using TAFF pipeline software, for compound 1 and compound 4 at the BP86/LANL2DZ//6-311++G (d,p) level of theory.

Compound	ϵ_{HOMO}	ϵ_{LUMO}	ΔE_{gap}	<i>I</i>	<i>A</i>	η	χ	ω
1	−4.33	−2.32	2.01	4.33	2.32	1.00	3.32	5.51
4	−4.68	−2.11	2.57	4.68	2.11	1.28	3.40	4.50

Validation, Formal analysis. **Sebastián Parra-Melipan**: Visualization, Validation, Formal analysis. **Pedro Aguirre**: Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: [The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Pedro Aguirre reports financial support was provided by University of Chile].

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Notes and references: ‡ CCDC-1981613 and CCDC-1981621 contain the supplementary crystallographic data for 1 and 4, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ica.2024.122064>.

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