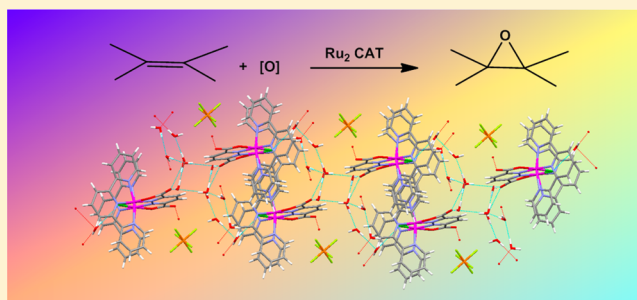


New Dinuclear Ruthenium Complexes: Structure and Oxidative Catalysis

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S Supporting Information

ABSTRACT: The synthesis of new dinuclear complexes of the general formula $\{[\text{Ru}^{\text{II}}(\text{trpy})_2(\mu\text{-pdz-dc})(\mu\text{-L})]^+\}$ [pdz-dc is the pyridazine-3,6-dicarboxylate dianion; trpy is 2,2':6',2''-terpyridine; L = Cl (1^+) or OH (2^+)] is described. These complexes are characterized by the usual analytical and spectroscopic techniques and by X-ray diffraction analysis. Their redox properties are characterized by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Complex 2^+ is used as the starting material to prepare the corresponding Ru-aqua complex $\{[\text{Ru}^{\text{II}}(\text{trpy})(\text{H}_2\text{O})_2(\mu\text{-pdz-dc})]^{2+}$ (3^{2+}), whose electrochemistry is also investigated by means of CV and DPV. Complex 3^{2+} is able to catalytically and electrocatalytically oxidize water to dioxygen with moderate efficiencies. In sharp contrast, 3^{2+} is a superb catalyst for the epoxidation of alkenes. For the particular case of *cis*- β -methylstyrene, the catalyst is capable of carrying out 1320 turnovers with a turnover frequency of 11.0 cycles min^{-1} , generating *cis*- β -methylstyrene oxide stereospecifically.



■ INTRODUCTION

Ruthenium complexes are attracting a great deal of attention because of their multiple applications in many fields of science.^{1–5} Polypyridyl ruthenium complexes are proposed as basic electronic devices because they can act as molecular wires and switches.^{6–8} They are also used as building blocks for the development of macromolecular assemblies,^{9–17} as well as for the design and construction of molecular machines.^{18–21} Furthermore, during the past decades, the application of ruthenium complexes as light harvesters in dye-sensitized solar cells^{22,23} has been a key issue for the development of new solar-energy conversion schemes.²⁴ Catalysis is also a field in which ruthenium complexes have broad applications given the rich chemistry of their complexes described that span in a broad range of oxidation states.^{25–32} A variety of reactions have been reported where ruthenium complexes behave as catalysts including nitrile hydrolysis, olefin metathesis, CO_2 reduction,^{33–44} and enantioselective hydrogenations.^{45–53} Ruthenium complexes are also excellent catalysts for oxidative transformations such as alcohol oxidation,^{54–62} epoxidation,^{63–72} sulfoxidation,^{73–76} and water oxidation.^{77–86} In these cases, the active site of the metal center is invariably a $\text{Ru}=\text{O}$ group where the metal is in a formal high oxidation state. Most of the literature related to redox catalysis using ruthenium complexes is based on mononuclear complexes because they are generally easily accessible from a synthetic viewpoint. This has fostered the preparation of families of related Ru-aqua complexes with different auxiliary ligands that have allowed an understanding of how their steric and

electronic perturbations influence the reactivity. We have set up a project to design dinuclear ruthenium complexes as redox catalysts containing a bridging ligand. The bridging ligand can act as an electronic communicator between the two metal centers or, depending on its nature, can act as an electronic insulator. Furthermore, the geometry of the ligand can allow two metals to cooperate through space. Therefore, a large number of complexes with different properties can be envisaged depending on the bridging ligand together with the rest of the auxiliary ligands filling up the first coordination sphere.

In the present paper, we report two new dinuclear ruthenium complexes of the general formula $\{[\text{Ru}(\text{trpy})_2(\mu\text{-pdz-dc})(\mu\text{-L})]^+\}$ [pdz-dc²⁻ is the pyridazine-3,6-dicarboxylate dianion; trpy is 2,2':6',2''-terpyridine; L = Cl (1^+) or OH (2^+); Table 1; see Scheme 1 for drawings of all of the ligands discussed in the present paper], and we use 2^+ as a catalyst precursor for oxidative transformations including alkene epoxidation and water oxidation. We have chosen the pdz-dc²⁻ ligand because the pyridazine moiety allows electronic communication between the ruthenium metals and thus generates a specific electronic coupling. Furthermore, its geometry allows the placement of two metals in very close proximity so that through-space interactions/cooperation can occur. Finally, the trpy ligand with its meridional geometry ensures the possibility of through-space interaction provided that there is no isomerization process toward the out isomers.

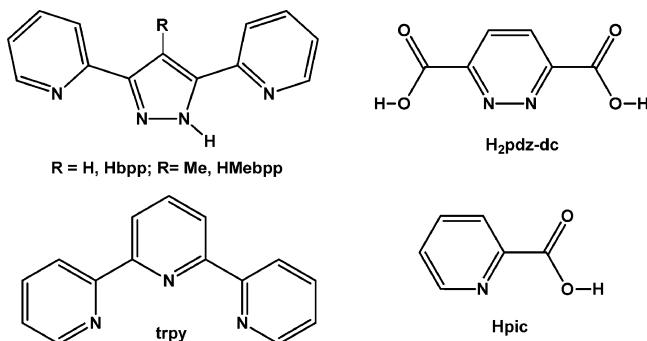
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Table 1. Crystal Data for Compounds 1⁺ and 2⁺

	1 ⁺	2 ⁺
empirical formula	C ₃₆ H ₃₈ ClF ₆ N ₈ O ₁₁ PRu ₂	C ₁₄₄ H ₉₇ F ₂₄ N ₃₂ O ₂₀ P ₄ Ru ₈
fw	1141.30	3983.98
temperature, K	296(2)	100(2)
wavelength, Å	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>n</i>
unit cell dimens		
<i>a</i> , Å	13.292(11)	16.0198(19)
<i>b</i> , Å	13.351(13)	34.255(5)
<i>c</i> , Å	14.855(14)	30.625(4)
α, deg	72.08(2)	90.00
β, deg	68.04(2)	97.256(4)
γ, deg	60.72(2)	90.00
volume, Å ³	2107(3)	16671(4)
<i>Z</i>	2	4
density (calcd), Mg m ^{−3}	1.799	1.587
abs coeff, mm ^{−1}	0.914	0.840
<i>F</i> (000)	1144	7892
cryst size, mm ³	0.06 × 0.04 × 0.02	0.2 × 0.1 × 0.02
θ range for data collection	1.50–25.40°	1.34–25.15°
index ranges	−15 ≤ <i>h</i> ≤ 15, −15 ≤ <i>k</i> ≤ 16, −17 ≤ <i>l</i> ≤ 17	−19 ≤ <i>h</i> ≤ 15, −40 ≤ <i>k</i> ≤ 25, −32 ≤ <i>l</i> ≤ 36
reflins collected	20779	62722
indep reflins	7231 [<i>R</i> (int) = 0.0961]	26196 [<i>R</i> (int) = 0.0844]
completeness to θ = 25.40°, %	0.933	0.878
abs corr	empirical	empirical
Max. and min transmission	0.98 and 0.81	1.00 and 0.92
refinement method	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²
data/restraints/ param	7231/21/628	26196/216/2106
GOF on <i>F</i> ²	0.978	0.950
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0471, <i>wR</i> 2 = 0.0989	<i>R</i> 1 = 0.0787, <i>wR</i> 2 = 0.1937
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0936, <i>wR</i> 2 = 0.1159	<i>R</i> 1 = 0.1552, <i>wR</i> 2 = 0.2174
largest diff peak and hole, e Å ^{−3}	1.064 and −0.877	1.067 and −0.876

Scheme 1. Ligands Used or Discussed in This Work



EXPERIMENTAL SECTION

Materials. All reagents used in the present work were obtained from Aldrich Chemical Co. or Alfa Aesar and used without further purification. Synthesis-grade organic solvents were obtained from SDS and routinely degassed with argon. Ethanol (EtOH) was dried with a 3.5 Å molecular sieves, and acetonitrile, dichloromethane (DCM),

hexane, and diethyl ether were used from SPS. High-purity deionized water was obtained by passing distilled water through a nanopure Milli-Q water purification system.

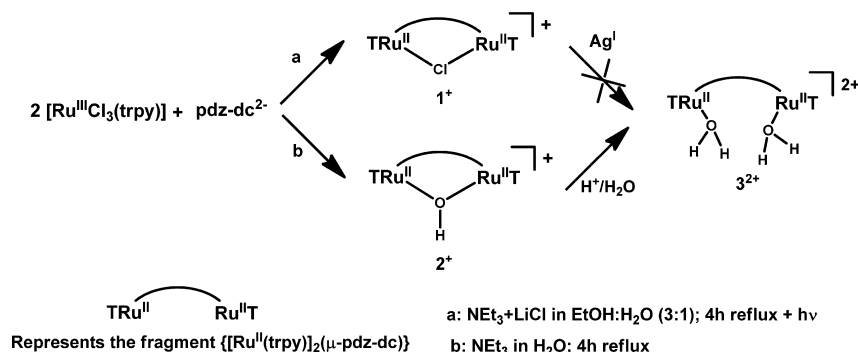
The sodium pyridazine-3,6-dicarboxylate⁸⁷ ligand (Na₂pdz-dc) and [Ru^{III}Cl₃(trpy)]⁸⁸ were prepared as described in the literature. All synthetic manipulations were routinely performed under an argon atmosphere using Schlenk and vacuum-line techniques.

{[Ru^{II}(trpy)]₂(μ-Cl)(μ-pdz-dc)}(PF₆)·6H₂O [1(PF₆)·6H₂O]. A total of 200 mg (0.454 mmol) of [RuCl₃(trpy)] and 130 mg (3.067 mmol) of LiCl were dissolved in 50 mL of a mixture of EtOH/water (3:1). A total of 133 μL (0.954 mmol) of triethylamine was added, and the mixture was stirred for 20 min at room temperature. A total of 10 mL of EtOH/H₂O (3:1) containing 48 mg (0.226 mmol) of sodium pyridazine-3,6-dicarboxylate sodium salt (Na₂pdz-dc) was added, and the mixture was heated at reflux for 4 h and then stirred in the presence of a 200 W tungsten lamp for 12 h. The resulting solution was filtered, and 1 mL of a saturated aqueous NH₄PF₆ solution was added. The precipitate formed was filtered and washed with DCM until it was a colorless filtrate. Recrystallization from acetone/ether yielded small dark-brown crystals. Yield: 56 mg (22%). Anal. Calcd for C₃₆H₃₈ClF₆N₈O₁₁PRu₂: C, 38.49; H, 3.23; N, 9.90. Found: C, 38.48; H, 2.98; N, 9.77. ¹H NMR (500 MHz, acetone-*d*₆): δ 8.94 (d, *J* = 5.4 Hz, 1H, H1–H15), 8.54 (d, *J* = 6.3 Hz, 2H, H7–H9), 8.52 (s, 1H, H17), 8.46 (d, *J* = 7.93 Hz, 2H, H4–H12), 8.08 (t, *J* = 8.0 Hz, 1H, H8), 7.99 (td, *J* = 7.9 and 1.5 Hz, 2H, H3–H13), 7.68 (ddd, *J* = 7.4, 5.5, and 1.4 Hz, 2H, H2–H14). ¹³C NMR (500 MHz, acetone-*d*₆): δ 159.3 (C20), 158.8 (C16), 158.3 (C5, C11, C6, C10), 154.5 (C1, C15), 138.1 (C3, C13), 135.5 (C8), 127.4 (C17), 127.8 (C2, C14), 124.0 (C4, C12), 122.5 (C7, C9). UV–vis [(CH₃)₂CO; λ_{max}, nm (ε, M^{−1} cm^{−1}): 420 (4695), 484 (4525), 536 (5038), 675 (1623). *E*_{1/2} (CH₃CN, V vs SSCE): 0.796 and 1.264. MALDI(+)-MS (CH₃CN): *m/z* 870.9 ([M – PF₆]⁺).

{[Ru^{II}(trpy)]₂(μ-pdz-dc)(μ-OH)}(PF₆)·4H₂O [2(PF₆)·4H₂O]. All of the syntheses have been carried out under a strictly argon atmosphere in a Schlenk line. A total of 400 mg (0.908 mmol) of [RuCl₃(trpy)] and 96 mg (0.453 mmol) of Na₂pdz-dc were dissolved in 50 mL of water. A total of 400 μL (2.869 mmol) of triethylamine was added, and the mixture refluxed for 4 h under argon. The solution was then filtered, and 1 mL of KPF₆ was added. A black solid precipitated after reduction of the volume. The dark solid obtained was washed with cold degassed acetone and dried under vacuum. Yield: 184 mg (38%). Anal. Calcd for C₃₆H₃₃F₆N₈O₉PRu₂: C, 40.46; H, 3.11; N, 10.48. Found: C, 40.38; H, 2.85; N, 10.43. ¹H NMR (400 MHz, acetone-*d*₆): δ 8.84 (d, *J* = 5.4 Hz, 2H, H22–36), 8.51 (s, 1H, H3), 8.33 (d, *J* = 8.1 Hz, 2H, H28–H30), 8.27 (d, *J* = 8.1 Hz, 2H, H25–H33), 7.87–7.75 (m, 3H, H3–H34–H29), 7.54 (dd, *J* = 7.5 and 5.6 Hz, 2H, H23–H35). ¹³C NMR (400 MHz, acetone-*d*₆): δ 171.7 (C1), 159.8 (C26–C32), 158.7 (C27–C31), 157.1 (C2), 154.3 (C22–C36), 137.5 (C24–C34), 133.7 (C29), 127.9 (C23–C35), 126.8 (C3), 123.8 (C25–C33), 121.9 (C28–C30). UV–vis [(CH₃)₂CO; λ_{max}, nm (ε, M^{−1} cm^{−1}): 277 (7871), 314 (8921), 421 (3826), 527 (3213), 560 (3238), 743 (1254). *E*_{p,a} (CF₃SO₃H, V vs SSCE): 0.290, 0.490, 0.680, 1.047. MALDI(+)-MS [(CH₃)₂CO/CH₂Cl₂]: *m/z* 852.2 ([M – PF₆]⁺).

Equipment and Measurements. All electrochemical experiments were performed in a PAR 263A EG&G or an IJ-Cambria CHI-660 potentiostat, using a three-electrode cell. A glassy carbon (GC) disk (3 mm diameter) or GC rod (Sigradur G, HTW, 7 mm diameter and 5 cm height) was used as the working electrode, a platinum wire as the auxiliary electrode, and SSCE as the reference electrode. Cyclic voltammograms were recorded at a 100 mV s^{−1} scan rate. The complexes were dissolved in previously degassed MeCN containing the necessary amount of (*n*-Bu₄N)(PF₆)(TBAH), used as the supporting electrolyte, to yield a 0.1 M ionic strength solution. All *E*_{1/2} values reported in this work were estimated from cyclic voltammetry (CV) as the average of the oxidative and reductive peak potentials (*E*_{p,a} + *E*_{p,c})/2 or from differential pulse voltammetry (DPV; pulse amplitude of 0.05 V, pulse width of 0.05 s, sampling width of 0.02 s, and pulse period of 0.1 s). In aqueous solutions, CV was run at pH = 1.0 in a 0.1 M triflic acid solution and at pH = 7.0 in a

Scheme 2. Synthetic Strategy



0.1 M phosphate buffer solution. Unless explicitly mentioned, the concentration of the complexes was approximately 1 mM.

400 MHz Bruker Avance II and Bruker Avance 500 MHz spectrometers were used to carry out NMR spectroscopy at room temperature. Samples were run in acetone- d_6 . The electrospray ionization and matrix-assisted laser desorption/ionization (MALDI) mass spectrometry (MS) experiments were performed on a Waters Micromass LCT Premier equipment and a Bruker Daltonics Autoflex equipped with a nitrogen laser (337 nm), respectively. UV-vis spectroscopy was performed on a Cary 50 Bio (Varian) UV-vis spectrophotometer with 1 cm quartz cells. For acid-base spectrophotometric titration, a 0.1 M buffered aqueous solution of the complex was used. The pH of the different solution was adjusted by adding small volumes (1 μL) of 4 M NaOH in order to produce a negligible overall volume change. Manometric measurements were performed with a homemade water-jacket glass reactor coupled to a Testo 521 manometer. The composition of the gaseous phase was determined by online MS with an OmniStar GSD 301 C (Pfeiffer) quadrupole mass spectrometer. In a typical experiment, 1 mL of a 1 mM complex solution in $\text{CF}_3\text{SO}_3\text{H}$ (pH = 1.0) was degassed with nitrogen until no oxygen could be detected. The reactor was then closed with a septum-sealed adapter. A 0.2 mL sample of a previously degassed $(\text{NH}_4)_2\text{Ce}^{\text{IV}}(\text{NO}_3)_6$ solution was then added directly into the reaction solution with a gastight Hamilton syringe. Blank experiments were performed by the addition of a $(\text{NH}_4)_2\text{Ce}^{\text{IV}}(\text{NO}_3)_6$ solution to neat $\text{CF}_3\text{SO}_3\text{H}$ (pH = 1.0) in the absence of catalyst. Epoxidation catalytic experiments were analyzed in an Agilent 6890N gas chromatograph coupled to a mass-selective detector with ionization by electronic impact and in an Agilent 6890 with a flame ionization detector using a HP5 column. In a typical experiment, the catalyst precursor $2(\text{PF}_6)$ (1.0 mM, 1.4 mg, 1.31×10^{-3} mmol), the alkene substrate (2.0 M, 2.62 mmol), the oxidant $\text{PhI}(\text{OAc})_2$ (4.0 M, 1.69 g, 5.25 mmol), and dodecane (165 mM, 50 μL , 0.22 mmol) as the internal standard are dissolved in DCM/EtOH (1:1) up to a total volume of the final volume of 1.2 mL. Then the solution is allowed to stir at room temperature for 30 min, and finally 94 μL of water (5.23 mmol) is added.

Reaction analysis is done as follows: an aliquot at the desired reaction time is taken, filtered through a Pasteur pipet filled with Celite, and eluted with diethyl ether and the filtrate analyzed by gas chromatography (GC). Identification of the reaction products was done by comparison with commercial products or by GC-MS. GC conditions: initial temperature, 40 $^\circ\text{C}$ for 10 min; ramp rate variable for each substrate, typically from 10 to 20 $^\circ\text{C min}^{-1}$; final temperature, 250 $^\circ\text{C}$; injection temperature, 220 $^\circ\text{C}$; detector temperature, 250 $^\circ\text{C}$. The yields of epoxide and substrate conversion were calculated with regard to the initial concentration of the substrate: conversion substrate = $\{[\text{substrate}]_{\text{initial}} - [\text{substrate}]_{\text{final}}\} / [\text{substrate}]_{\text{initial}} \times 100$; yield epoxide = $\{[\text{epoxide}] / [\text{substrate}]_{\text{initial}}\} \times 100$; selectivity for epoxide = $[\text{yield epoxide} / \text{conversion substrate}] \times 100$.

Single-Crystal X-ray Structure Determination. *Crystal Preparation.* Crystals for $1(\text{PF}_6)$ were grown by the slow evaporation of a water solution of the complex. Crystals for complex $2(\text{PF}_6)$ were grown by the slow evaporation of an acetonitrile solution of the

complex. All measured crystals were prepared under inert conditions immersed in perfluoropolyether as the protecting oil for manipulation.

Data Collection. Crystal structure determinations for $1(\text{PF}_6)$ and $2(\text{PF}_6)$ were carried out using a Bruker-Nonius diffractometer equipped with an APEX 2 4K CCD area detector, a FR591 rotating anode with Mo $K\alpha$ radiation, Montel mirrors as a monochromator, and an Oxford Cryosystems Cryostream 700 Plus low-temperature device ($T = -173$ $^\circ\text{C}$). Full-sphere data collection was used with ω and φ scans. Programs used: data collection, APEX-2;⁸⁹ data reduction, Bruker SAINT V/6.0A;⁹⁰ absorption correction, SADABS⁹¹ or TWINABS.⁹²

Structure Solution and Refinement. A crystal structure solution was achieved using direct methods, as implemented in *SHELXTL*⁹³ and visualized using the program *XP*. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F^2 using all measured intensities was carried out using the program *SHELXTL*. All non-hydrogen atoms were refined including anisotropic displacement parameters. In order to avoid highly disordered solvent molecules, the program *SQUEEZE*⁹⁴ was used.

The ORTEP plot of $2(\text{PF}_6)$ was drawn with an occupancy of 30%. The asymmetric unit contains four independent molecules of the complex, four PF_6^- anions, and 32 different positions of disordered water molecules. In order to avoid the highly disordered solvent molecules, the program *SQUEEZE* was applied, leading to a refined model with a R1 value of 7.87%. One of the PF_6^- anions is also disordered in two positions with a ratio of 83:17. In one of the complex molecules, a hydrogen atom corresponding to a bridging hydroxide ligand was localized.

RESULTS AND DISCUSSION

Synthesis, Structure, and NMR Spectroscopy. The synthetic strategy followed for the preparation of the complexes described here is depicted in Scheme 2. The addition of the octahedral ruthenium complex $[\text{Ru}^{\text{III}}\text{Cl}_3(\text{trpy})]$ to the N_2O_2 compartmental dinucleating pdz-dc^{2-} ligand in the presence of NEt_3 and LiCl generates the corresponding dinuclear ruthenium complex $\{[\text{Ru}^{\text{II}}(\text{trpy})]_2(\mu\text{-Cl})(\mu\text{-pdz-dc})\}^+$ (1^+) bridged by both the pdz-dc^{2-} and chlorido ligands. The 22% yield obtained in this reaction is low, mainly because of the parallel formation of $[\text{Ru}^{\text{II}}(\text{trpy})_2]^{2+}$ that could not be avoided. Multiple attempts to remove the Cl-bridged ligand and generate the corresponding aqua complex $\{[\text{Ru}^{\text{II}}(\text{trpy})(\text{H}_2\text{O})]_2(\mu\text{-pdz-dc})\}^{2+}$ (3^{2+}) from 1^+ failed. In the absence of Cl^- and using neat water as the solvent, the reaction of $[\text{Ru}^{\text{III}}\text{Cl}_3(\text{trpy})]$ and pdz-dc^{2-} afforded the hydroxido-bridged complex $\{[\text{Ru}^{\text{II}}(\text{trpy})]_2(\mu\text{-pdz-dc})(\mu\text{-OH})\}^+$ (2^+) also in low yields for the same reason as that in the previous case. The acidic treatment of 2^+ in water generates the desired aqua complex, as indicated in eq 1.

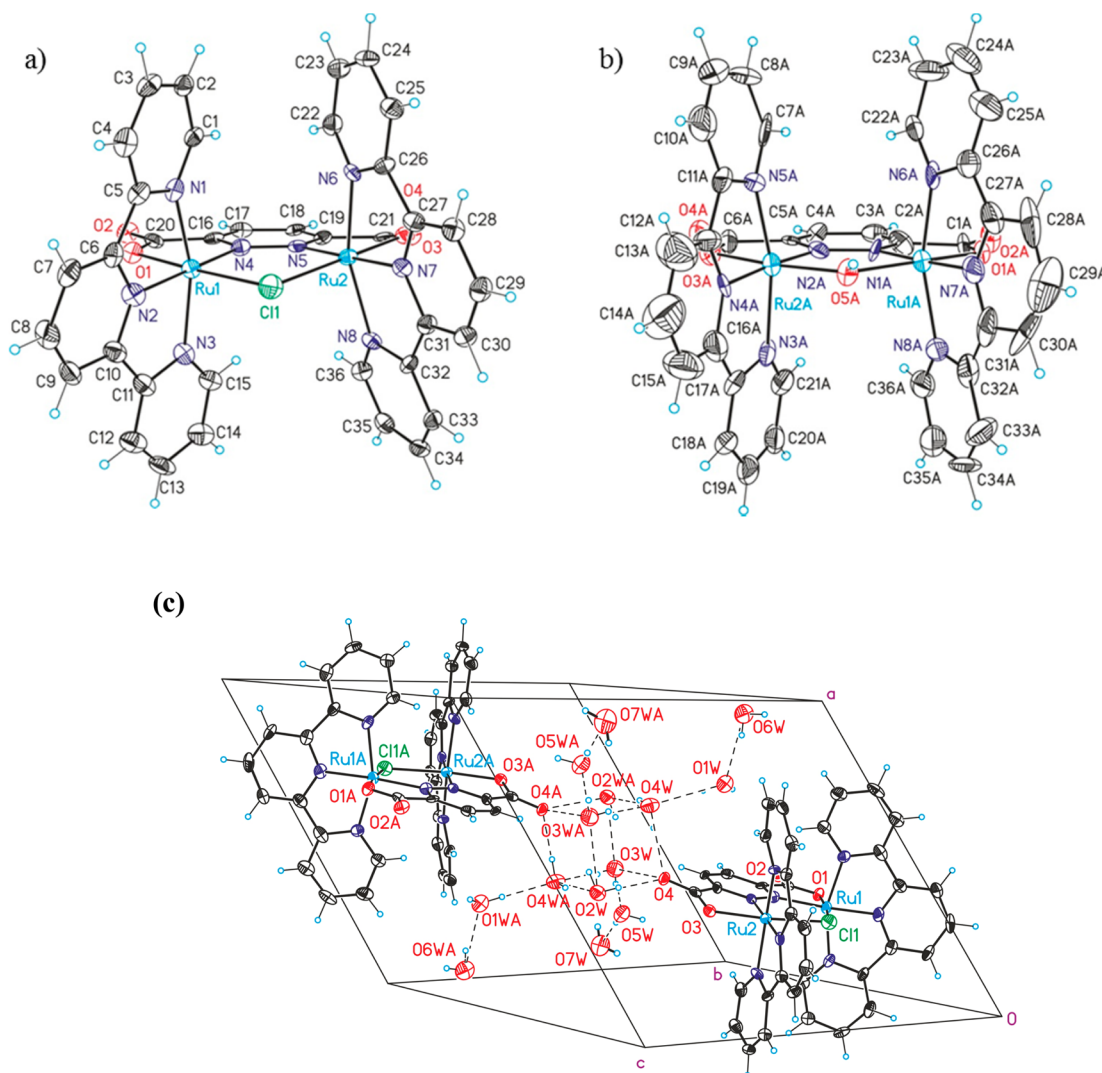
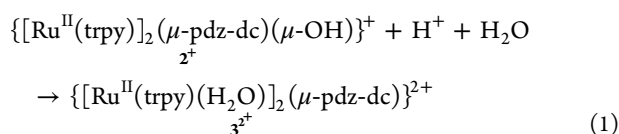


Figure 1. ORTEP plot of the X-ray crystal structure of the cationic moieties of (a) 1^+ (ellipsoid at 50% probability) and (b) 2^+ (ellipsoid at 30% probability), together with the labeling scheme. Selected bond lengths (Å) and angles (deg) for 1^+ : Ru1–N1, 2.067(6); Ru1–N2, 1.976(5); Ru1–N3, 2.060(6); Ru1–N4, 2.032(5); Ru1–O1, 2.077(4); Ru1–Cl1, 2.357(2); Ru1–Cl1–Ru2, 100.81(10). Selected bond lengths (Å) and angles (deg) for 2^+ , Ru1A–N6A, 2.037(9); Ru1A–N7A, 1.952(8); Ru1A–N8A, 2.071(9); Ru1A–N1A, 1.985(7); Ru1A–O1A, 2.074(6); Ru1A–O5A, 2.080(6); Ru1A–O5A–Ru2A, 110.4(3). (c) Molecular packing arrangement of 1^+ , showing the formation of a distorted cubanelike structure with nonbonding oxygen atoms (O4 and O4A) from the pdz-dc $^{2-}$ ligand and solvation water molecules. Color code: Ru, cyan; N, navy blue; O, red; Cl, green; C, black; H, light blue.



Complexes 1^+ and 2^+ were characterized by the usual spectroscopic techniques as well as by X-ray diffraction analysis. Figure 1 displays an ORTEP plot for the cationic moiety of these two complexes together with their corresponding atom-labeling scheme. CIF files are presented as Supporting Information (SI).

In both complexes, the ruthenium centers adopt a distorted octahedral geometry with bond distances and angles comparable to those of analogous complexes reported earlier in the literature.^{81,95–103} An interesting feature here is the Ru–N–N–Ru torsion angles of 7.08° for 1^+ and of 3.21° for 2^+ (N–N are the nitrogen atoms of the pdz-dc $^{2-}$ ligand), which reflect the need for the pdz-dc $^{2-}$ ligand to adapt to the longer Ru–Cl

distance (2.357 Å)^{81,104,105} with regard to that of the bridging Ru–OH distance (2.089 Å). This is also responsible for a longer Ru–Ru distance for the chlorido complex 1^+ (3.636 Å)^{81,105,106} with regard to the hydroxido complex 2^+ (3.431 Å).

In order to adapt to this geometrical constraint, rotation of the carboxylate moiety out of the pyridazine plane occurs, placing the ruthenium metal center also out of this plane. This is reflected in the N5–C19–C21–O3 torsion angle of 10.9° for 1^+ , whereas for 2^+ , the related torsion angle (N1A–C2A–C1A–O1A) is only of 1.7°. As a consequence of all this, the molecular structure of 2^+ is very close to C_{2v} symmetry, with the C_2 axis going through the OH bridge and bisecting the pyridazine moiety of the pdz-dc $^{2-}$ ligand, whereas 1^+ has strictly no symmetry elements except for E . The molecular packing arrangement adopted by complex 1^+ is very interesting and is exhibited in Figure 1c. In the figure, the unit cell where two cationic moieties of 1^+ are hydrogen-bonded by several water molecules is shown. A cubane type of structure is generated

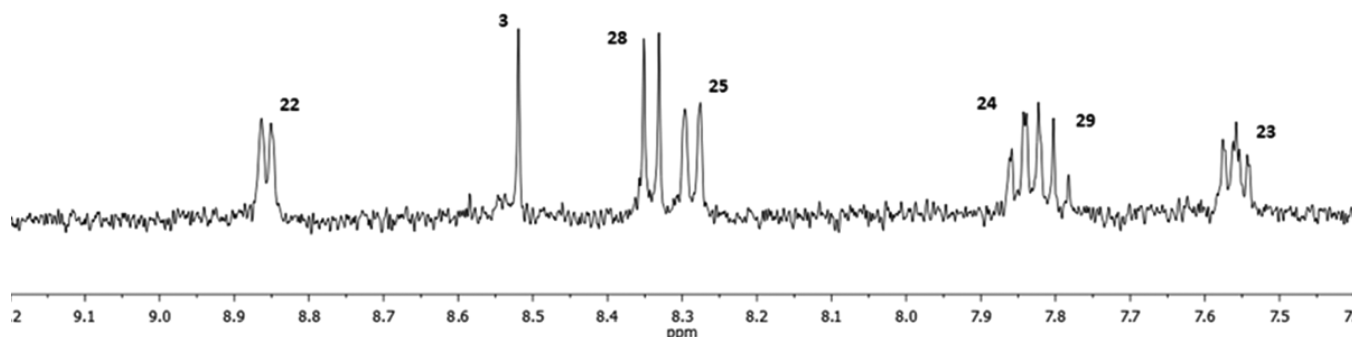


Figure 2. ^1H NMR spectra recorded in acetone- d_6 for 2^+ . The labeling scheme is given in the X-ray structure.

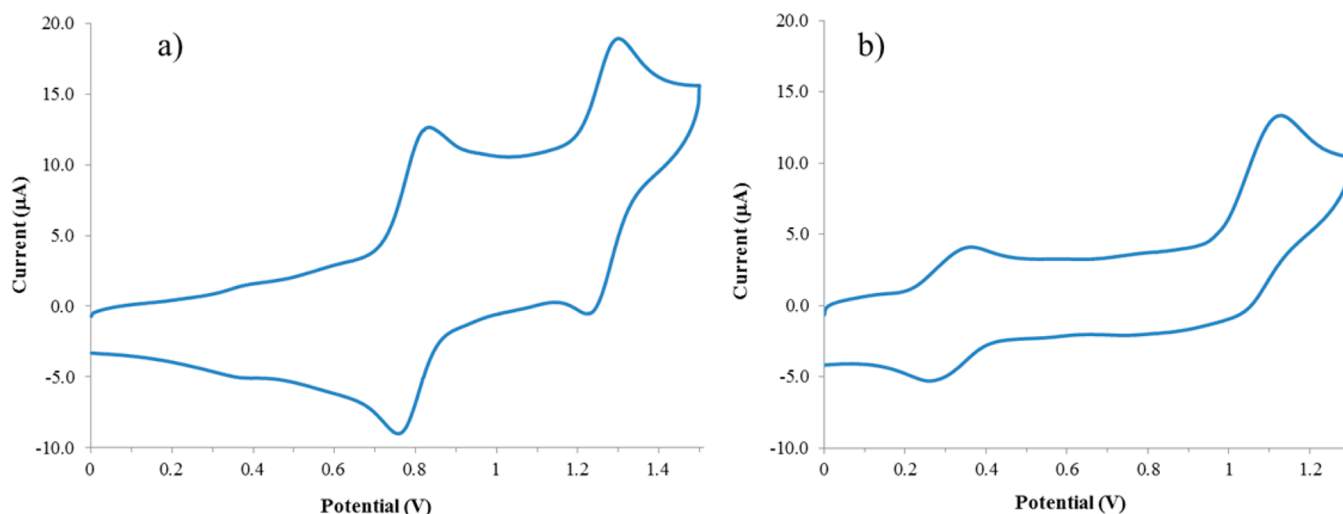


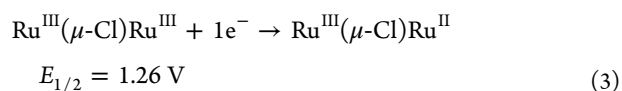
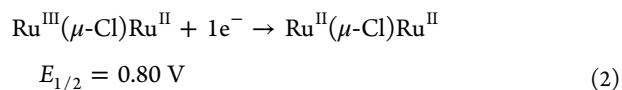
Figure 3. CV images of 1^+ (a) and 2^+ (b) in MeCN (0.1 mM TBAH). A GC disk was used as the working electrode, a platinum wire as the auxiliary electrode, and SSCE as the reference electrode. Cyclic voltammograms started at 0.0 V, and the scan rate was 100 mV s^{-1} .

where six of its vertices are occupied by oxygen atoms of the hydrogen-bonded water molecules and the remaining two oxygen atoms come from noncoordinated oxygen atoms (O4) belonging to the carboxylate moiety of the pdz-dc^{2-} ligand from two symmetry-related 1^+ units, which are situated on opposite vertices. Additional water molecules are further connected via hydrogen bonding to the cubane structure. Finally, the other carboxylate of the pdz-dc^{2-} ligand is also hydrogen-bonded with an additional water molecule that is not shown in the drawing.^{106–108}

1D and 2D NMR spectroscopy for complexes 1^+ and 2^+ was carried out in acetone- d_6 . The ^1H NMR spectrum of 2^+ is displayed in Figure 2, whereas the rest of the spectra are presented as Supporting Information (Figures S1–S3). All of the resonances displayed in Figure 2 could be unambiguously assigned based on their multiplicity and integrals and thanks to the 2D spectra. As can be observed in the spectrum, in solution 2^+ acts as if it has C_{2v} symmetry, as is the case in the solid state. For the chlorido bridging complex 1^+ , the spectrum obtained is also consistent with 1^+ having C_{2v} symmetry because of the fast interconversion of conformers at room temperature.^{109,110}

Redox Properties and Electrocatalytically Active Species. The redox properties of the complexes described in the present work were investigated by means of CV and DPV and are reported in Figures 3–5. The cyclic voltammograms of 1^+ and 2^+ in MeCN (0.1 M TBAH) at 100 mV s^{-1} scan rate versus SSCE are exhibited in Figure 3. As can be observed in the figure, complex 1^+ presents two chemically reversible redox

waves at $E_{1/2} = 0.80\text{ V}$ ($\Delta E_p = 59\text{ mV}$) and $E_{1/2} = 1.26\text{ V}$ ($\Delta E_p = 59\text{ mV}$) that are assigned to the following one-electron processes:



It is striking to compare these potentials with the ones obtained for the related complex $\{[\text{Ru}^{\text{II}}(\text{trpy})]_2(\mu\text{-Cl})(\mu\text{-Mebpp})\}^{2+}$ [4^{2+} , where Mebpp is the 2,2'-(4-methyl-1H-pyrazolate-3,5-diyl)dipyridine monoanionic ligand; see Scheme 1 for the drawing], which has a similar structure but the pdz-dc^{2-} dianionic ligand is replaced by the monoanionic Mebpp $^-$.¹¹¹ For the latter, these potentials are anodically shifted and appear at 0.67 and 1.12 V, respectively. The anodic shift for 1^+ with regard to 4^{2+} is unexpected and potentially indicates that, in this particular case, the carboxylate moiety of the pdz-dc^{2-} ligand is strongly hydrogen-bonded by the solvent and, as a consequence, generates a charge delocalization of the carboxylates over the network hydrogen-bonded water molecules. As a consequence of this, the monoanionic Mebpp $^-$ ligand ends up being a better electron donor to the ruthenium metal center than the dianionic pdz-dc^{2-} ligand. This hydrogen-bonding effect is also in agreement with the extensive hydrogen bonding

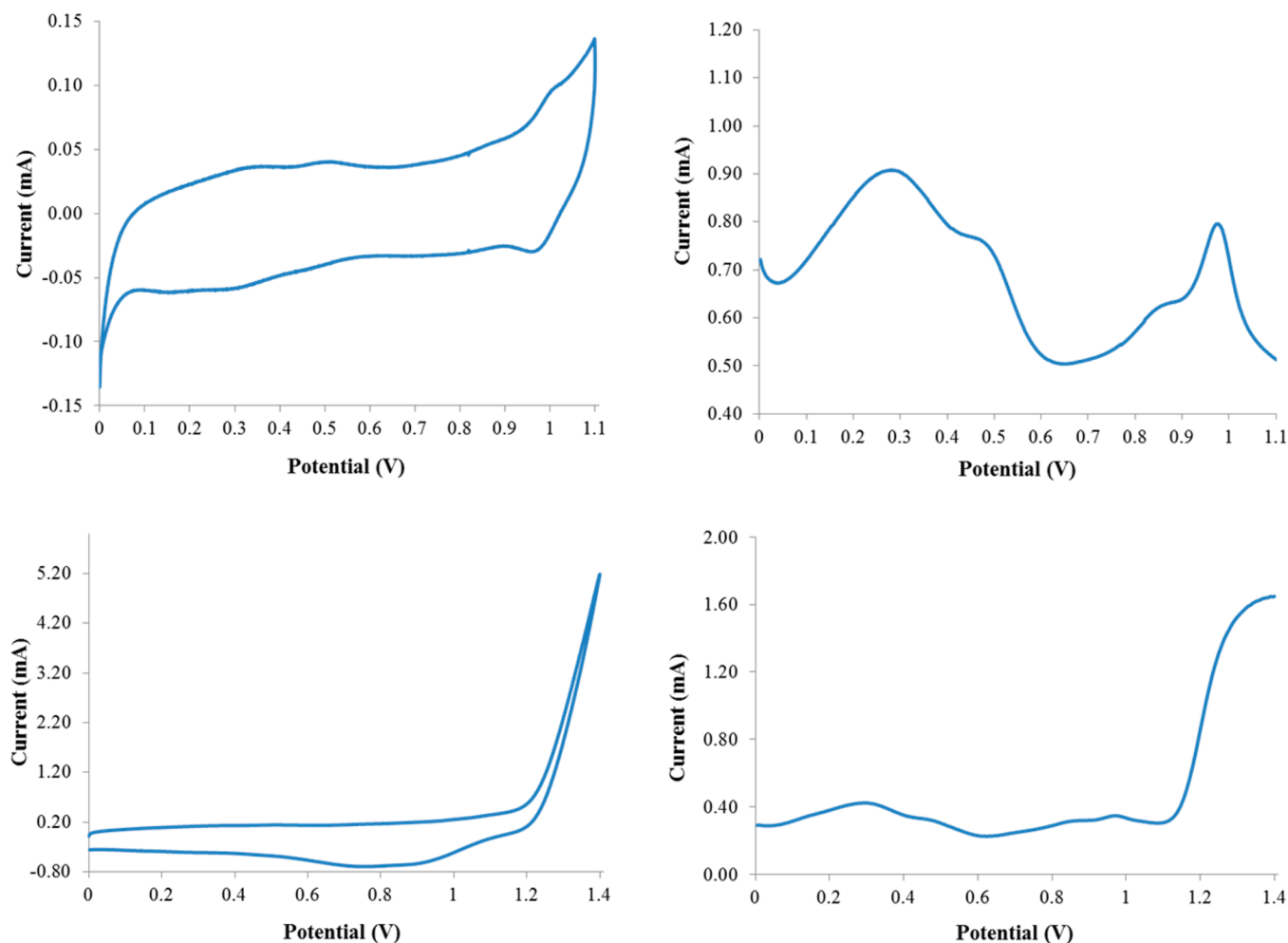


Figure 4. CV (left) and DPV (right) images at different potential ranges for 3^{2+} at pH = 1.0 in a 0.1 M triflic acid aqueous solution: (top) up to 1.1 V; (bottom) up to 1.4 V. The scan starts at 0.0 V in all cases with a scan rate of 100 mV s^{-1} . A GC rod was used as the working electrode, a platinum wire as the auxiliary electrode, and SSCE as the reference electrode.

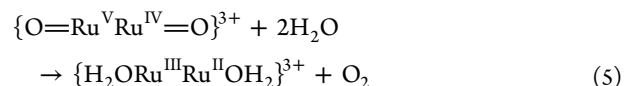
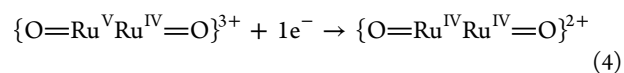
observed in the solid-state structure for 1^+ through a number of water molecules that was discussed in the previous section.

The CV image of 2^+ in MeCN shows a reversible wave at $E_{1/2} = 0.25 \text{ V}$ ($\Delta E = 80 \text{ mV}$) and a chemically irreversible wave at $E_{1/2} = 1.05 \text{ V}$, as can be observed in Figure 3. $\Delta E_{1/2}$ defined as the III,III/III,II–III,II/II,II potentials are 740 mV for 2^+ and 530 mV for 1^+ , which under comparable conditions is indicative of a stronger electronic coupling between the metal centers for 2^+ with regard to 1^+ . The comproportionation constants (III,III + II,II $\rightarrow$ 2III,II) that can be deduced for these redox potentials are $K_c = 9.1 \times 10^8$ for 1^+ and $K_c = 3.22 \times 10^{12}$ for 2^+ .^{1f2,113} This is in agreement with a much stronger magnetic coupling obtained for related dinuclear copper complexes bridged by hydroxido units with regard to similar ones bridged by chlorido ligands.^{114–119}

The electrochemistry of 3^{2+} has been investigated at pH = 1.0 in a 0.1 M triflic acid aqueous solution using 2^+ as the precursor (see eq 1), and its CV and DPV images are presented in Figure 4. Four redox processes are observed within the potential range of 0.0–1.10 V, which are tentatively assigned to the redox couples shown in Table 2 based on related complexes previously described in the literature.⁸¹ As can be seen in the table, in this case a cathodic shift is observed upon comparison of the potentials of 3^{2+} with regard to those of the related Hbpp complex $\{[\text{Ru}^{\text{II}}(\text{trpy})(\text{H}_2\text{O})_2(\mu\text{-bpp})]^{3+}\}$ (5^{3+}). This cathodic

shift is also in agreement with the higher $\text{p}K_{\text{a,II,II}}$ for 3^{2+} (9.2; see the equation in the SI) with regard to 5^{3+} (6.8)⁸¹ because of the much higher σ -donation capacity of the pdz-dc²⁻ ligand compared to bpp[−] (the trpy and pdz-dc ligands are not shown).

If the potential is scanned up to 1.4 V, a large anodic electrocatalytic current (E at the onset of the peak is approximately 1.2 V; Figure 4, bottom) is observed in CV that is associated with a further one-electron oxidation of the complex concomitant with the electrocatalytic oxidation of water to dioxygen, in agreement with eqs 4 and 5.



CV of 3^{2+} was also carried out at pH = 7.0 and is shown in Figure 5a. The redox potentials extracted from this CV image are displayed in Table 2 together with those of 5^{3+} for comparison purposes. CV of 3^{2+} was also run in the presence of styrene (Figure 5b), and an increase of the current intensity is observed at roughly 0.75 V, which is consistent with electrocatalytic oxidation of styrene to styrene oxide according to the following equations:

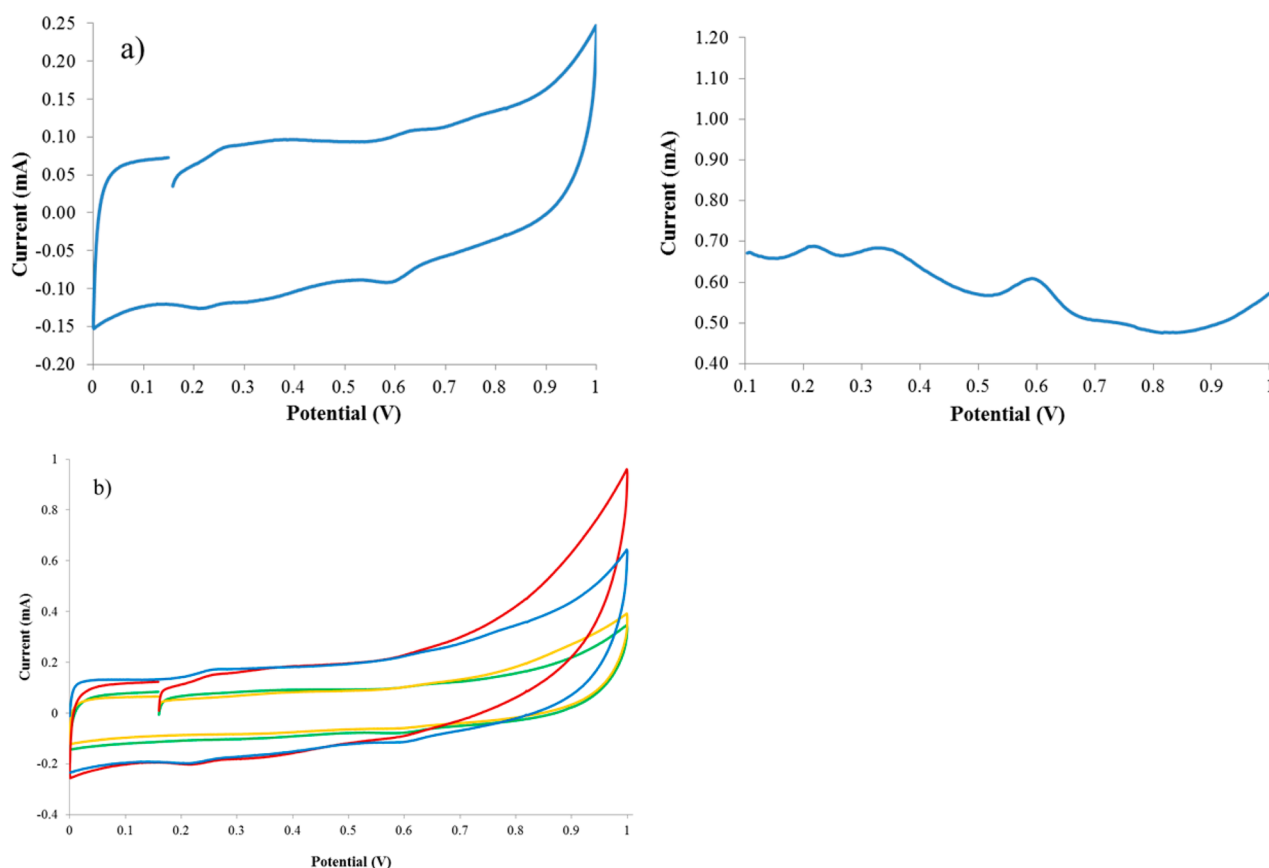
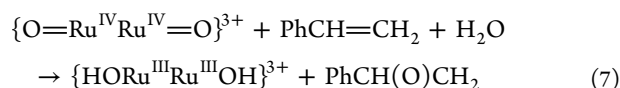
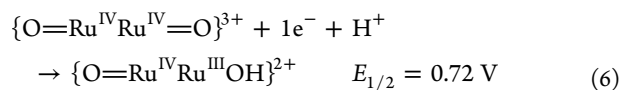


Figure 5. (a) CV (left) and DPV (right) images of 3^{2+} in a pH = 7.0 phosphate buffer solution. (b) CV images of 3^{2+} (1 mM) in a pH = 7.0 phosphate buffer (blue line) and of 3^{2+} (1 mM) in the presence of styrene (60 mM, red line). Blanks: styrene (60 mM, orange line) and a bare carbon electrode (green line). Starting scan at 0.15 V for all except 3^{2+} (blue line), which starts at 0.0 V. A GC rod was used as the working electrode, a platinum wire as the auxiliary electrode, and SSCE as the reference electrode.

Table 2. Redox Potentials (V vs SSCE) for 1^+ , 2^+ , and 4^{2+} in MeCN (0.1 M TBAH) for 3^{2+} and 5^{3+} at pH = 1.0 and 7.0^a

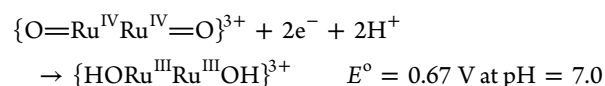
complex	pH	$E_{1/2}$				ref
		III,II–II,II	III,III–III,II	IV,III–III,III	IV,IV–IV,III	
$\{[\text{Ru}^{\text{II}}(\text{trpy})_2(\mu\text{-Cl})(\mu\text{-pdz-dc})]^+(1^+)\}$		0.80	1.26			tw
$\{[\text{Ru}^{\text{II}}(\text{trpy})_2(\mu\text{-pdz-dc})(\mu\text{-OH})]^+(2^+)\}$	0.25		1.05			tw
$\{[\text{Ru}^{\text{II}}(\text{trpy})_2(\mu\text{-Cl})(\mu\text{-Mebpp})]^{2+}(4^{2+})\}$	0.67		1.12			111
$\{[\text{Ru}^{\text{II}}(\text{trpy})(\text{H}_2\text{O})_2(\mu\text{-bpp})]^{3+}(5^{3+})\}$	1.0	0.59	0.65	0.88	1.10	81
	7.0	0.28	0.52			
$\{[\text{Ru}^{\text{II}}(\text{trpy})(\text{H}_2\text{O})_2(\mu\text{-pdz-dc})]^{2+}(3^{2+})\}$	1.0	0.28	0.48	0.86	0.98	tw
	7.0	0.21	0.33	0.59	0.73	

^apH = 1.0 is a 0.1 M triflic acid aqueous solution; pH = 7.0 is a 0.1 M phosphate buffer.



Given the two-electron nature of the oxidation of alkenes to their corresponding epoxide, it is interesting to keep in mind

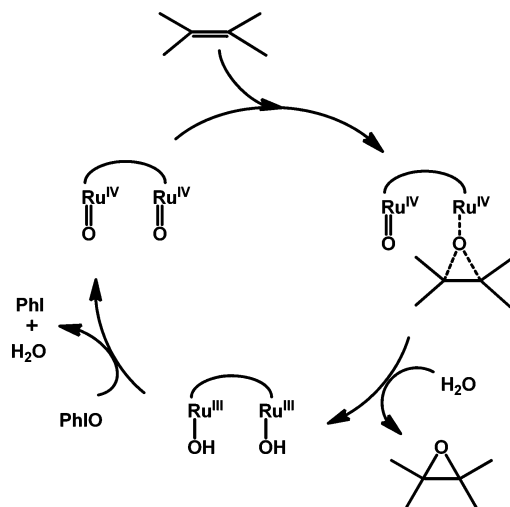
the thermodynamic driving force of the catalyst for a two-electron transformation calculated from the respective one-electron processes $[(\text{IV,IV} \rightarrow \text{VI,III}) + (\text{IV,III} \rightarrow \text{III,III})/2]$, as indicated in the following equation:



All of the above is consistent with the catalytic cycle presented in Scheme 3, where the applied potential is substituted by PhIO, a chemical oxidant that regenerates the active species and that will be further discussed in the next section.

Chemically Induced Oxidative Catalysis. The catalytic activity of 3^{2+} was tested with regard to its capacity to oxidize water and alkenes. The addition of cerium(IV) to an acidic solution of 3^{2+} generates bubbles immediately because of the formation of molecular oxygen, which was monitored manometrically and by online MS. In particular, a 0.94 mM 3^{2+} /94 mM cerium(IV)/0.1 M triflic acid aqueous solution up to a total volume of 1.20 mL generates 5.66 μmol of oxygen that represents a turnover number (TN) of 5 and a turnover frequency (TOF) of 0.77 cycles min^{-1} calculated during the first 60 s (see Figure S5 in the SI). This represents a discrete 20% efficiency with regard to the added cerium(IV). The further addition of cerium(IV) does not generate more oxygen, indicating that the catalyst is dead after the first addition and that the reaction that generates molecular oxygen runs parallel with the one that deactivates the catalyst. Oxidation efficiencies

Scheme 3. Proposed Catalytic Cycle



can be significantly improved up to 44.5% when the Ox/Cat ratio is decreased to 25 using 24 mM cerium(IV) and keeping the rest of the conditions identical. Online MS under the same conditions as the manometric experiments confirmed the oxygen nature of the gas generated in these reactions. No CO₂ was detected. In addition, blank experiments were carried out that showed that, in the absence of 3²⁺, no dioxygen was formed.

The catalytic activity of 3²⁺ toward the epoxidation of alkenes has been initially tested and optimized for the oxidation of styrene and the reaction evolution monitored by GC and GC–MS. The results obtained for all of the alkenes tested are gathered in Table 3. As can be observed in entry 1, the system 1.0 mM 2(PF₆)/2.0 M styrene/4.0 M PhI(OAc)₂/4.0 M H₂O in DCM/EtOH (1:1) gives 0.88 M styrene oxide, which represents 880 TNs with regard to the initial catalyst in 5 h. After this time, the conversion of the initial substrate is 87% and thus represents an epoxide selectivity of 51%. The water added to the system is needed to favor the generation of PhIO

from PhIOAc₂¹²⁰ and to transform our catalyst precursor 2⁺ into catalyst 3²⁺, as described in previous sections.

The activity of 3²⁺ for the epoxidation of a variety of alkenes is remarkable, and the results are reported in entries 2–5 of Table 3. For instance, the system 3²⁺/*cis*-β-methylstyrene generates an impressive 1.32 M *cis*-β-methylstyrene oxide that represents a TN of 1320 with regard to the epoxide with an initial turnover frequency (TOF_i) of 11.0 cycles min^{−1} (see entry 3 in Table 3). It is interesting here to compare the performance of *trans*-[Ru^{II}(pic)(trpy)(H₂O)]⁺ (6⁺, where pic is the pyridyl-2-carboxylato monoanionic ligand; see Scheme 1 for the drawing) with that of 3²⁺ because the former can be considered a mononuclear analogue of the latter. Under conditions identical with those for 3²⁺, 6⁺ gives a yield of 26% of *cis*-β-methylstyrene epoxide after 2 h and a maximum value of 65%, with full conversion of the substrate, after more than 25 h.¹²¹ Additionally 3²⁺ is about 5 times faster than its mononuclear homologue 6⁺; this fact suggests a potential cooperation effect between the two metal centers for the dinuclear 3²⁺ catalyst. The capacity of the two metal centers to electronically communicate with each other via the pyrazolato moiety for the bpp[−] ligand in ruthenium complexes has been shown previously.¹¹¹ Potentially, one of the Ru=O groups can be responsible for oxygen-atom transfer to the alkene, while the second Ru=O group can fix the substrate via hydrogen bonding with the alkene, as indicated in Scheme 3. We have also previously shown this type of through-space interaction in related complexes with similar geometry.¹¹⁰

An additional glance at Table 3 shows that with electron-donor groups the catalyst 3²⁺ performs much better than with electron withdrawers. Thus, cyclohexene (entry 5; Figure 6) is the best, whereas *cis*-stilbene (entry 4) is the worst. The latter also suffers from potential steric effects because of the bulkiness of the two phenyl rings. The electronic effects are in agreement with the electrophilic character of the Ru^{IV}=O active group proposed in the electrochemical section. Another interesting feature of the systems studied here is the stereospecific nature of the catalysis performed in the sense that no *cis*/*trans* isomerization takes place for the *cis*-alkenes (entries 3 and 4). This points toward a mechanism of either a concerted oxygen-

Table 3. Catalytic Performance of 3²⁺ for the Epoxidation of Several Alkenes Using PhI(OAc)₂ as the Oxidant in a 1:2000 Catalyst/Substrate Ratio

Entry	Alkene	Subs. Conv.(%) ^b	[Epox], M; (Sel. %) ^c	TN/TOF ^d
1	Styrene	87	0.88 (51)	880/17.3
2	<i>trans</i> -β-methylstyrene	93	1.47 (79) ^e	1470/15.7
3	<i>cis</i> -β-methylstyrene	92	1.32 (72) ^f	1320/11.0
4	<i>cis</i> -stilbene	48	0.32 (36) ^f	320/0.4
5	Cyclohexene	100	1.58 (79)	1580/40.6

^aReaction conditions: 2(PF₆) (1.0 mM, 1.4 mg, 1.31 × 10^{−3} mmol), substrate (2.0 M, 2.62 mmol), PhI(OAc)₂ (4.0 M, 1.69 g, 5.25 mmol), H₂O (4.0 M, 94 μL, 5.23 mmol), and dodecane (165 mM, 50 μL, 0.22 mmol) in DCM/EtOH (1:1) up to a total volume of the final volume of 1.3 mL. ^bSubs. Conv. (%) is the substrate conversion calculated according to ([Subs]₀ − [Subs]_t)/[Subs]₀ × 100. ^cEpox. Sel. (%) is the epoxide selectivity calculated according to ([epoxide]_t/([Subs]₀ − [Subs]_t)) × 100. ^dTN is the turnover number with regard to epoxide only. TOF_i is the initial turnover frequency expressed as the number of epoxidation catalytic cycles per minute. ^e100% of *trans*-epoxide. ^f100% of *cis*-epoxide.

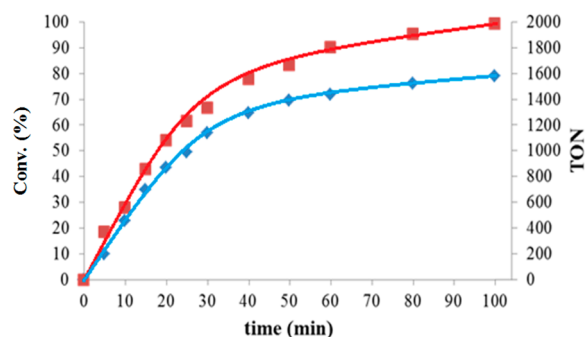


Figure 6. Evolution profile for the consumption of cyclohexene in percent (red line, left y axis) and the formation of cyclohexene oxide in TON (blue line, right y axis) for catalyst 3^{2+} , under the conditions indicated in Table 3.

atom transfer from the $\text{Ru}^{\text{IV}}=\text{O}$ active site to the double bond of the alkene or a radical path were C–C rotation of the generated radical is much slower than the ring closing that generates the final epoxide.^{122–126} Overall, a summary of the proposed catalytic cycle is depicted in Scheme 3. Further mechanistic work is in progress in our laboratories to unfold the elemental steps that take place in the epoxidation catalytic cycle and to fully understand the potential cooperative effects in the dinuclear catalysts.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional spectroscopic, electrochemical, and kinetic data. CCDC 923043 & 923044 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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