

## Reactivity of trinuclear ruthenium acetates with nitrite and nitric oxide ligands in aqueous media

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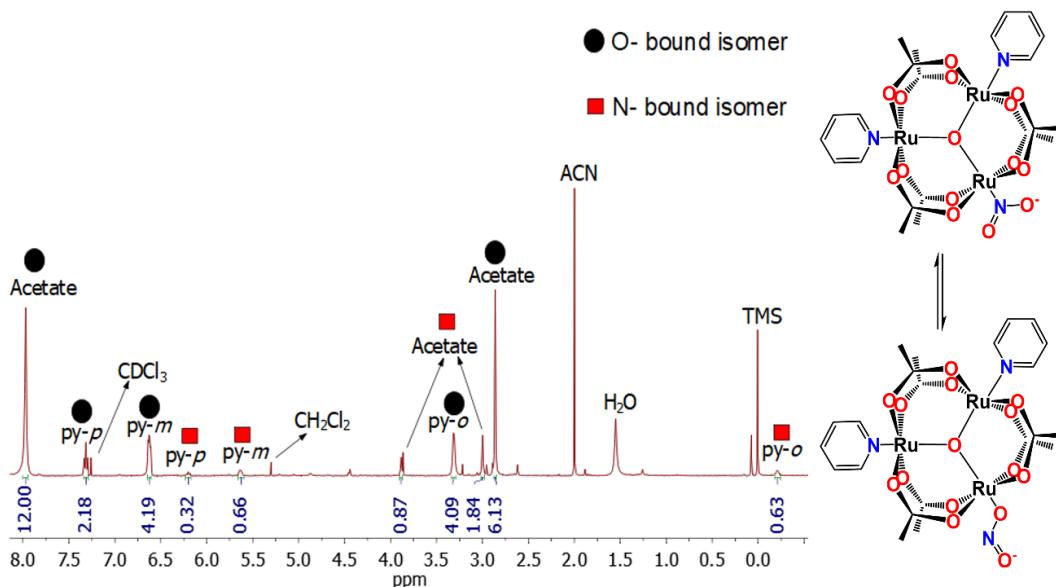
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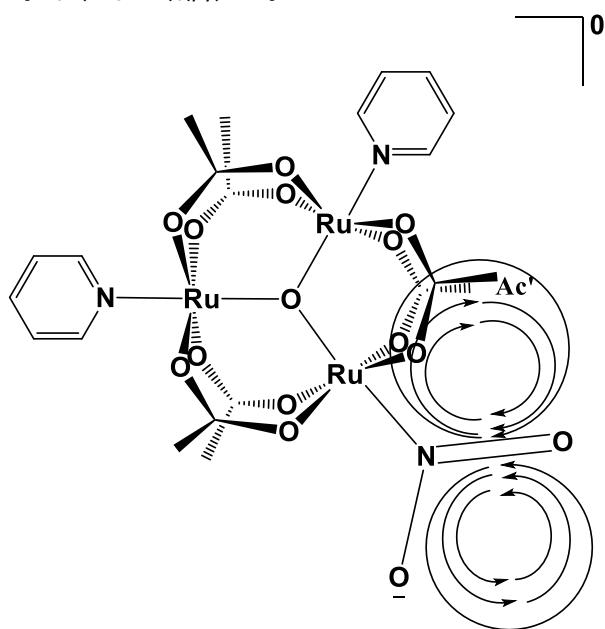
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### Support Information

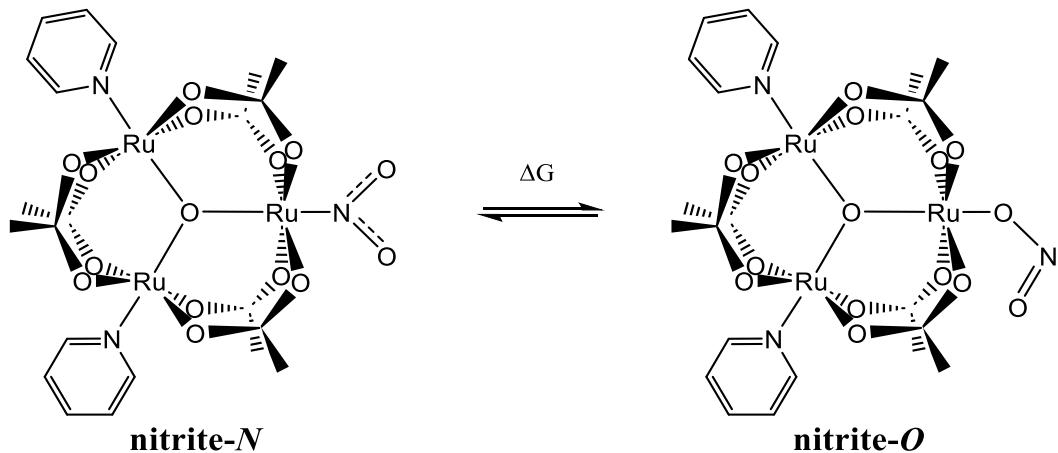
**Figure S1.**  $^1\text{H}$  NMR spectrum of a  $1 \times 10^{-2}$  mol.L<sup>-1</sup> solution of the compound  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2\text{NO}_2]$  in  $\text{CDCl}_3$ , 400 MHz, 298K.



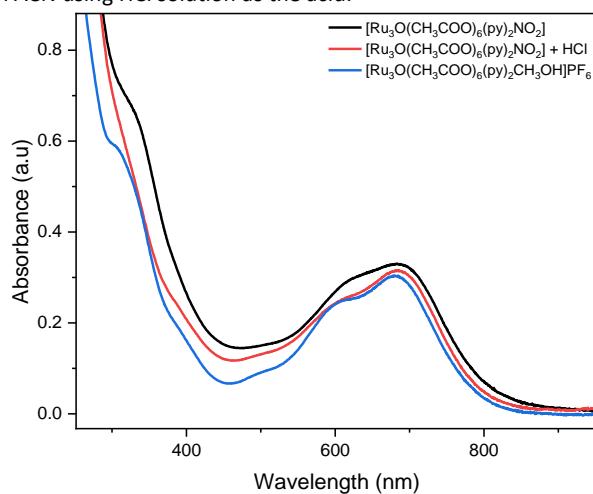
**Figure S2.** Schematic representation of induced magnetic field generated by electron circulation in the nitrite-N linkage isomer of compound  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2\text{NO}_2]$ .



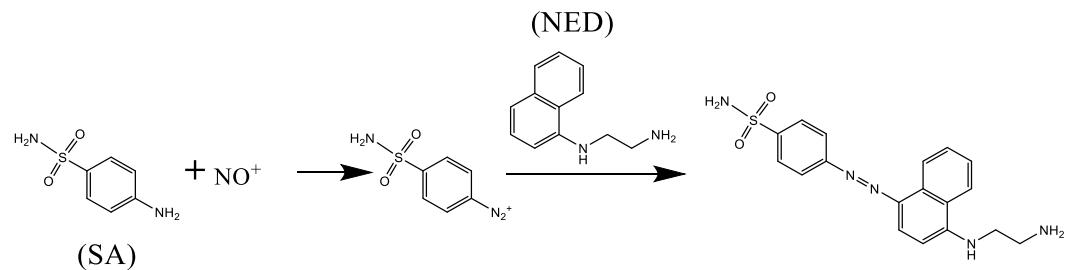
**Figure S3.** Interconversion equilibrium of the linkage isomers of the complex  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2\text{NO}_2]$ .



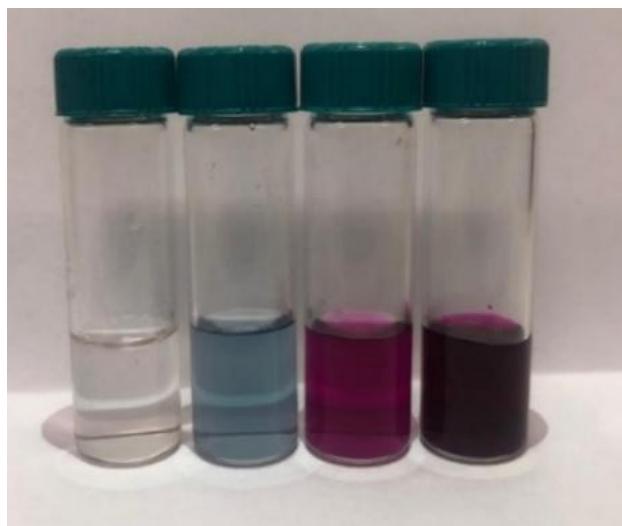
**Figure S4.** Comparison between the absorption spectra of the compound  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2\text{CH}_3\text{OH}]\text{PF}_6$  and the spectra obtained during the acid-base reactivity experiment of the complex  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2\text{NO}_2]$  ( $4.45 \times 10^{-5}$  mol.L<sup>-1</sup>) with the complex in ACN using HCl solution as the acid.



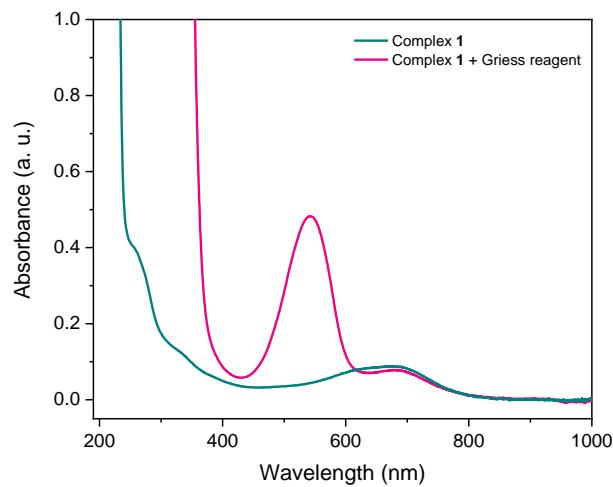
**Figure S5.** Schematic representation of the chemical reactions involved in the Griess test.



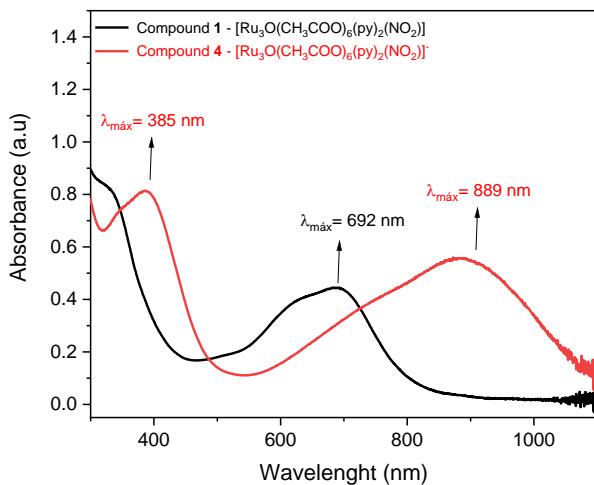
**Figure S6.** Photograph showing the color change during the experiment using Griess reagent for complex  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2\text{NO}_2]$  (**1**). From left to right solutions of: Reagent, Complex **1**, Complex **1** + reagent, and positive control ( $\text{NaNO}_2$ ).



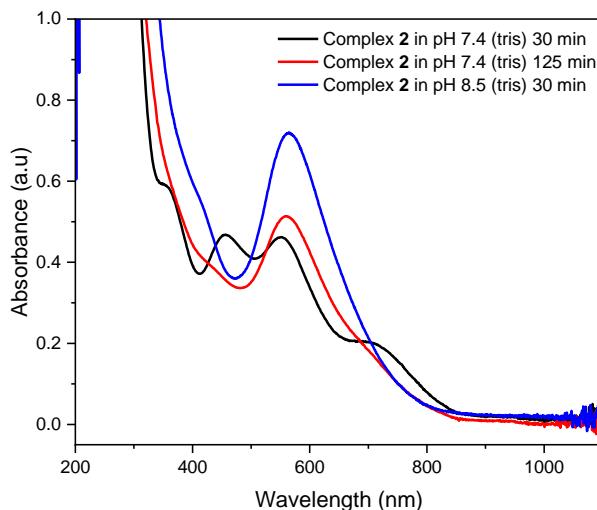
**Figure S7.** Electronic absorption spectra of complex  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2\text{NO}_2]$  in aqueous solution with 2% DMSO before and after addition of Griess reagent.



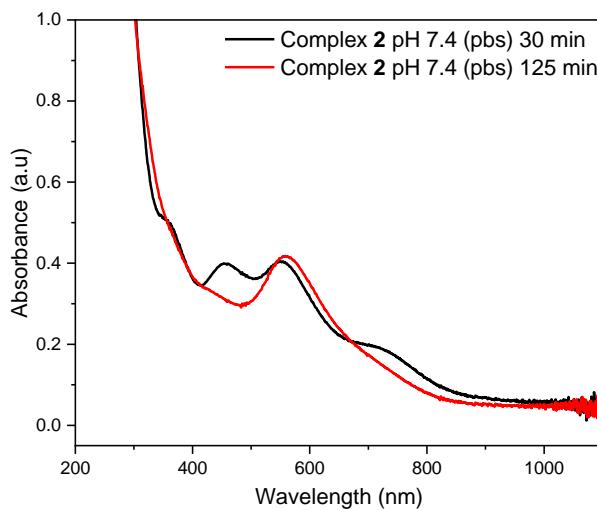
**Figure S8.** Comparison of the electronic absorption spectra of the compound  $[\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2(\text{NO}_2)]$  with  $[\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2(\text{NO}_2^-)]$  reduced with hydrazine in DMSO.



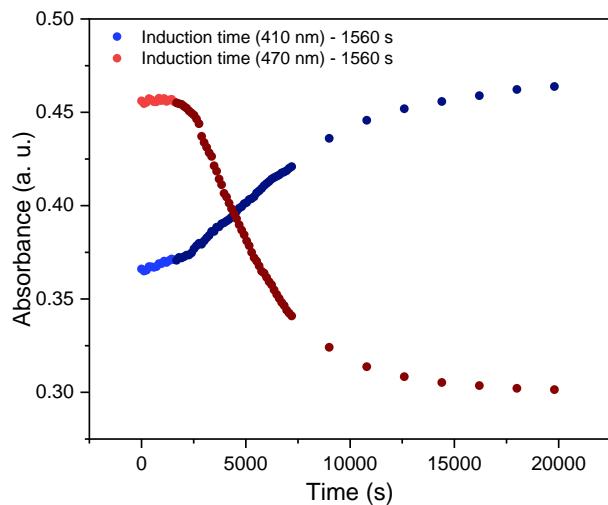
**Figure S9.** Electronic absorption spectra of complex  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2\text{NO}]PF_6$  **2** in tris.HCl buffer solution at pH 7.4 and 8.5 after 30 minutes and after production of **3**.



**Figure S10.** Electronic absorption spectra of the  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2\text{NO}]PF_6$  **2** complex in PBS buffer solution at pH 7.4 after 30 minutes and after the production of **3** (125 s).



**Figure S11.** Kinetic curve obtained from the reactivity of the  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2\text{NO}]^{\text{PF}_6}$  **2** complex in tris.HCl buffer solution pH 7.4 with its respective induction time of 1560 s.



**Figure S12.** Kinetic curve obtained from the reactivity of the  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2\text{NO}]^{\text{PF}_6}$  **2** complex in tris.HCl buffer solution pH 8.5 with its respective induction time of 600 s.

