

## Report on the outcomes of a Short-Term Scientific Mission<sup>1</sup>

Action number: CA20129

Grantee name: Cauê Paula de Souza

### **Details of the STSM**

Title: Bond-selected dissociation of polyhapto ruthenium precursors for photo-assisted nanofabrication: Insights from theory

Start and end date: 31/08/2024 to 15/09/2024

### **Description of the work carried out during the STSM**

Description of the activities carried out during the STSM. Any deviations from the initial working plan shall also be described in this section.

(max. 500 words)

The tasks foreseen in the initial plan were successfully accomplished with additional outcomes. During the first two days, discussions about the foundation of the EDA-NOCV analysis and its capabilities were carried out. Dr Zlatar offered several exemplary case studies from his previous and current works to illustrate and inspire our own investigation. This was followed by a brainstorming session wherein we outlined the plan for the PACVD precursors to be investigated in this work. As an outcome of this discussion, it became clear that the study of a series of other analogue polyhapto ruthenium complexes was a promising endeavour to pursue in a standalone derivative work. We also brought to Dr Zlatar's appreciation and critical evaluation the results of our previous TD-DFT analysis of the systems. Some subsequent analysis was recommended to enrich our results. During the subsequent days, EDA-NOCV calculations were performed on the systems already synthesised and investigated by McElwee-White *et al.* [1], as well as on part of the newly proposed molecules. The results were partially analysed and discussed. Several evaluations of the method's accuracy were carried out, including the influence of basis sets, DFT exchange-correlation functional, and DFT integration grid quality. Access to resources, means of communication, and extension of the collaborative work were planned and will be secured on the aftermath of this STSM.

[1] C. R. Brewer, N. C. Sheehan, J. Herrera, A. V. Walker, L. McElwee-White, *Organometallics* **2022**, *41*, 761–775.

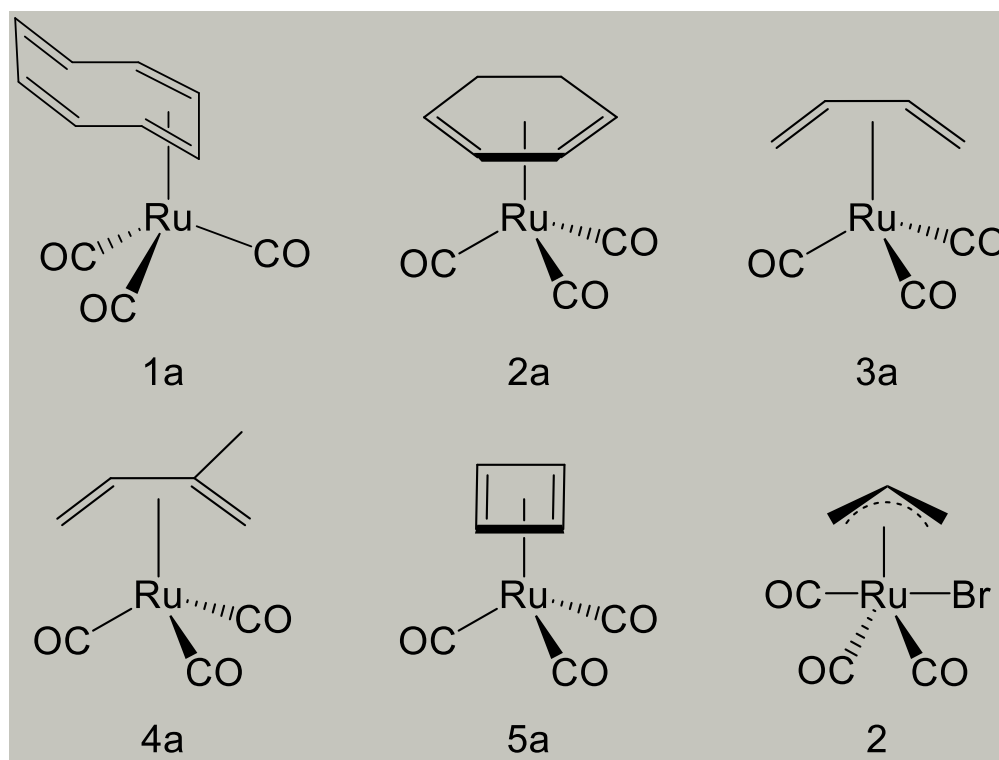
<sup>1</sup> This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

## Description of the STSM main achievements and planned follow-up activities

Description and assessment of whether the STSM achieved its planned goals and expected outcomes, including specific contribution to Action objective and deliverables, or publications resulting from the STSM. Agreed plans for future follow-up collaborations shall also be described in this section.

(max. 500 words)

The initial set of PACVD precursors under investigation consists of the molecules depicted in Figure 1. The molecule containing the cyclobutadiene (CBD) ligand (**5a**) has already shown great resistance to lose its diene ligand in comparison to the others [1]. The EDA-NOCV analysis carried out in this work showed, through the orbital interaction energies, that the description of the Ru-diene bonding in this molecule is better if we consider the CBD as a triplet neutral moiety bonded to the remaining Ru(CO)<sub>3</sub> moiety, also neutral and triplet. The same description is correct for the Ru-cyclooctatetraene bonding (**1a**). Conversely, for all the other η<sup>4</sup> molecules (**2a–4a**), the partitioning of the Ru-diene bonding is better described if the fragments are both neutral and *singlet* (see Table 1). This result parallels the different experimental behaviour aforementioned.



**Figure 1** – Series of initial PACVD precursors already synthesised and tested experimentally to be analysed in this work.

**Table 1** – EDA-NOCV orbital interaction energies (kcal.mol<sup>-1</sup>) for two different partitioning of the Ru-polyhapto ligand bonds in molecules **1a** through **5a** (see Figure 1). The less negative the values, the better the description of the bonding scheme.

	1a-COTRu	2a-CHDRu	3a-BuDRu	4a-iPentDRu	5a-CBuDRu
<b>Neutral Triplet</b>	<b>-191.23</b>	-201.55	-204.52	-204.75	<b>-196.38</b>
<b>Neutral Singlet</b>	-204.99	<b>-199.71</b>	<b>-198.29</b>	<b>-199.53</b>	-259.21

In view of such results, we hypothesised that the difference could be associated with a geometrical effect. Both the CBD and cyclooctatetraene (COT) ligands have a π-orbital distribution arranged in a square-

like geometry, whereas the remaining ligands exhibit a less symmetrical  $\pi$ -orbital distribution. To explore this possibility further, we plan to perform a scan starting with the complex containing the butadiene (BD) ligand (**3a**) in its equilibrium geometry, gradually deforming the BD ligand into the square geometry of the CBD ligand. At each step, we will carry out EDA-NOCV analysis, tracking the orbital interaction energies for both the neutral singlet and neutral triplet partitioning of the fragments.

Besides the molecules rendered in Figure 1, we decided to perform a systematic EDA-NOCV investigation of 1–7 hapticity series. Specifically, we are analysing (polyhapto)Ru(CO)<sub>n</sub> complexes ranging from  $\eta^1$  to  $\eta^7$  hapticities considering the smallest acyclic and cyclic polyhapto ligands. This investigation will form a separate body of work from the analysis discussed above and has already been initiated during the course of this STSM, with plans to continue and complete it in the coming weeks.

In total, this STSM will produce two publications from the immediate results and the subsequent developments, with potential for future collaboration held in eager consideration from both parts. We hope that the investigations set during this mission will enlighten our understanding of the photochemistry of polyhapto-ruthenium-based complexes, aiding in the molecular design of better PACVD precursors, ultimately advancing the actual deposition and nanofabrication technique to industrial application (WG1's Task T1.3 and WG2's Task T2.4). The insights gained from this research will also aid in the development of multiscale simulations of the PACVD process (WG3's Task T3.4). The result of this STSM is expected to be disseminated to the broader scientific community both as publications and presentation in conferences, as well as potential training of new users of the EDA-NOCV technique at the University of Kent (WG4 T4.1, T4.4). Therefore, we consider that this STSM surpassed the expected outcomes.

- [1] C. R. Brewer, N. C. Sheehan, J. Herrera, A. V. Walker, L. McElwee-White, *Organometallics* **2022**, *41*, 761–775.