

Report on the outcomes of a Short-Term Scientific Mission¹

Action number: CA20129

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Details of the STSM

Title: Copper catalysts for controlled radical photopolymerization

Start and end date: 31/08/2024 to 14/09/2024

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.

The objectives outlined in the original plan were successfully met. During the first two days, we thoroughly explored the fundamentals of EDA-NOCV analysis and examined its various applications through detailed discussions. Dr Zlatar shared numerous case studies from his past and ongoing research, offering both illustrative examples and valuable inspiration for our project. We then collaborated to develop a comprehensive strategy for investigating the copper complexes central to this project. Through these discussions, it became evident that the open-shell nature of the complexes, combined with the presence of two bidentate ligands, introduced significant complexity in the application of EDA-NOCV. As a result, it was determined that various isomers of the complexes must be considered, alongside different fragmentations of the system. In the subsequent days, EDA-NOCV calculations were performed on the proposed copper complex systems. Preliminary results were analysed and discussed, focusing on the method's accuracy and the influence of basis sets. Additionally, alternative fragmentation schemes were explored, adjusting individual multiplicities and removing virtual orbitals to better understand the systems' properties and behaviour. Finally, we outlined plans for continued collaboration, detailing resource access, communication channels, and the extension of the project beyond this STSM.

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.

The complexes studied are depicted in Figure 1, illustrating both the *cis* and *trans* configurations. The key differences between these complexes are found in the central part of the ligands, which consist either

¹This 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.

of a benzimidazole or imidazole group, and the *para* substituent on the aromatic ring attached to one of the nitrogen atoms. For the fragment analysis, we defined one fragment as the ligand (lf) and the other as the metal centre with the remaining ligand (mf). The first aspect examined was the electron distribution within the fragments of the *trans*-**Pmb** complex (Table 1), maintaining a net charge of zero and a multiplicity of two, as the entire system exists as a doublet. This complex was chosen due to the wealth of experimental data available, a higher electron count in the central part of the ligand, and the simplicity of its *para* substituent, which is a hydrogen atom. Additionally, the *trans* geometry was selected because previous studies have shown that it offers greater stability than the *cis* configuration.

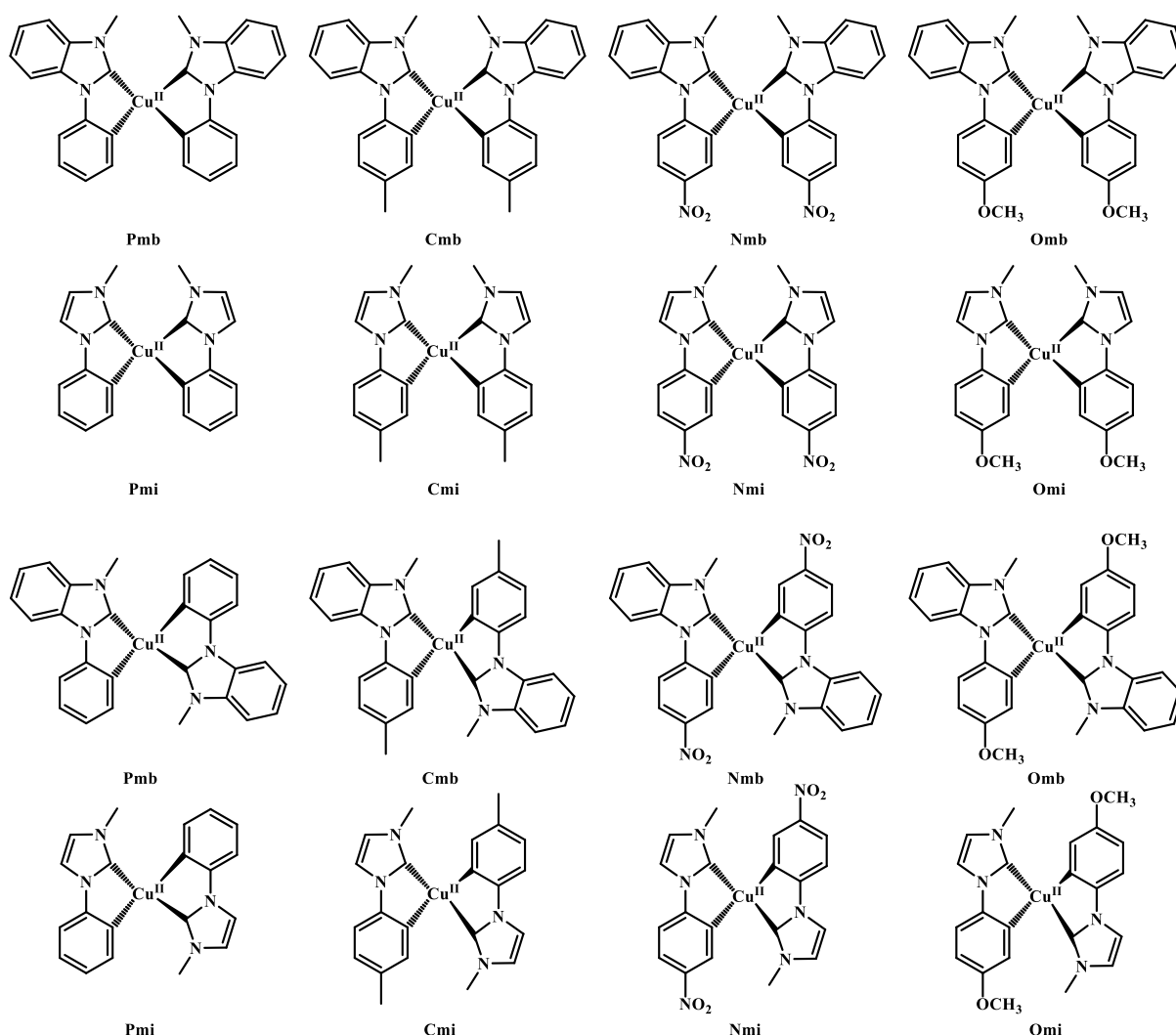


Figure 1 – Series of copper complexes analysed in this work.

Table 1 – EDA-NOCV orbital interaction energies (kcal.mol⁻¹) for all fragments considered for *trans*-**Pmb**. The data as divided in lf / fm. The less negative the values, the better the description of the bonding scheme. Red: best bonding description overall. Bold: best bonding description considering charged fragments.

| Combination Charges | d / s | d / t | d / s os | s / d | s os / d | t / q | t / d |
|------------------------|----------------|---------|----------|----------------|----------|---------|---------|
| 0 / 0 | -121.36 | -227.46 | -270.59 | --- | | | |
| -1 / +1 | --- | | | -128.10 | -189.68 | -289.63 | -176.68 |

*q: quartet, t: triplet, d: doublet, s: singlet, os: open shell.

As shown in Table 1, the EDA-NOCV analysis conducted in this study demonstrated that the Cu-ligand bonding description is more accurate when treating the ligand fragment (fl) as a neutral doublet and the metal-ligand fragment (fm) as a neutral singlet, based on the orbital interaction energies. The interaction energies for the alternative description, where fl is considered a singlet anion and fm a doublet cation, were also relatively low. As a result, all other complexes were analysed using both combinations, as outlined in Table 2. The same bonding pattern observed for the **Pbm** complex applies to the other complexes, further supporting that the neutral singlet/neutral doublet model offers a more accurate representation of the bonding in these copper complexes.

Table 2 – EDA-NOCV orbital interaction energies (kcal.mol⁻¹) for all complexes. The data as divided in fl / fm. The less negative the values, the better the description of the bonding scheme.

| Complex | Combination | | d / s | s / d |
|------------|--------------|--------------|---------|---------|
| | <i>cis</i> | <i>trans</i> | | |
| Pmb | <i>cis</i> | | -115.96 | -127.79 |
| | <i>trans</i> | | -121.36 | -128.10 |
| Pmi | <i>cis</i> | | -113.30 | -121.38 |
| | <i>trans</i> | | -117.33 | -119.97 |
| Cmb | <i>cis</i> | | -115.58 | -128.18 |
| | <i>trans</i> | | -118.23 | -125.88 |
| Cmi | <i>cis</i> | | -112.80 | -121.81 |
| | <i>trans</i> | | -116.13 | -130.15 |
| Nmb | <i>cis</i> | | -116.63 | -127.55 |
| | <i>trans</i> | | -120.29 | -125.67 |
| Nmi | <i>cis</i> | | -113.83 | -121.51 |
| | <i>trans</i> | | -117.84 | -120.43 |
| Omb | <i>cis</i> | | -115.94 | -127.36 |
| | <i>trans</i> | | -120.74 | -127.90 |
| Omi | <i>cis</i> | | -113.62 | -121.64 |
| | <i>trans</i> | | -115.61 | -120.18 |

With the fragment combination established, we sought to understand the differences between the geometries. Initially, we analysed the bonding angles; however, since all complexes exhibited a seesaw geometry, this did not offer distinctive insights. We then focused on four key factors: Pauli repulsion, electrostatic interaction, total orbital interaction, and dispersion. The data revealed two distinct patterns. In the first group—**Pmi**, **Pmb**, **Omb**, and **Omi**—the *trans* configuration exhibited higher Pauli repulsion due to the fragments being closer together. However, this was offset by stronger electrostatic and orbital interactions, making the *trans* geometry more favorable due to its covalent interactions. The second group—**Cmb**, **Cmi**, **Nmb**, and **Nmi**—featuring weak activator and strong deactivator groups, respectively, displayed lower Pauli repulsion in the *trans* configuration, indicating the fragments are farther apart. This reduced electrostatic interaction was balanced by stronger total orbital interactions.

Further studies are planned to deepen our understanding of these systems. This STSM is expected to lead to at least one publication based on the immediate results, with ongoing developments offering significant potential for future collaboration. We hope that the research initiated during this mission will advance our understanding of the photochemistry of copper-NHC complexes. Additionally, the insights gained will further establish EDA-NOCV as a valuable tool for bonding analysis in organometallic chemistry and reinforce the role of DFT calculations in elucidating key aspects of the electronic structure of these systems. The outcomes will be disseminated through publications and conference presentations and could lead to training opportunities for new users of the EDA-NOCV technique at the University of Kent (WG4 T4.1, T4.4). Given these results, we believe this STSM has surpassed our initial expectations.