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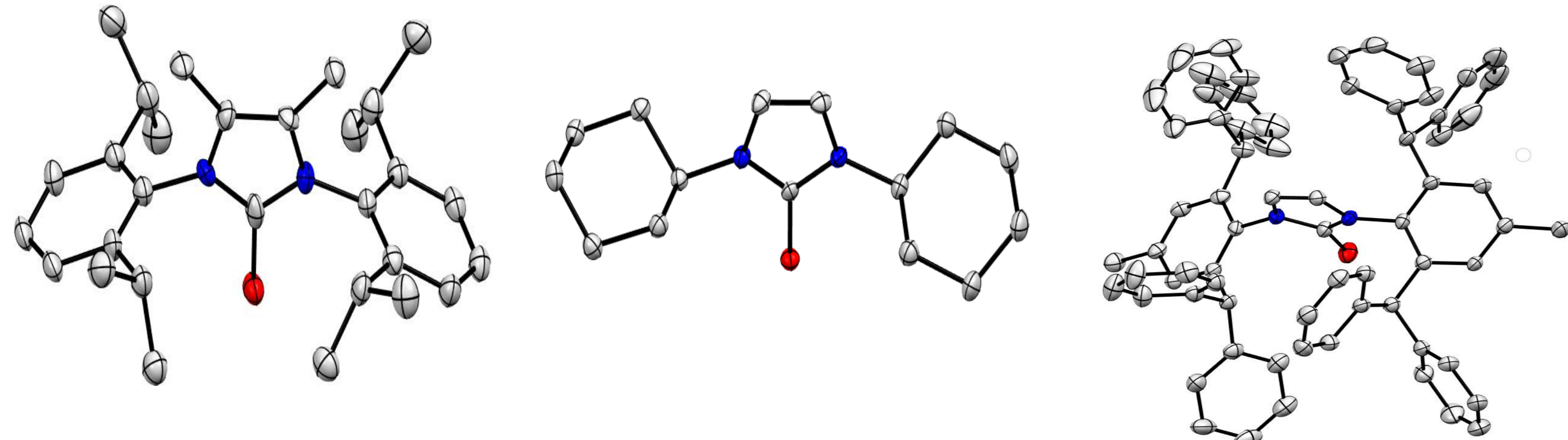
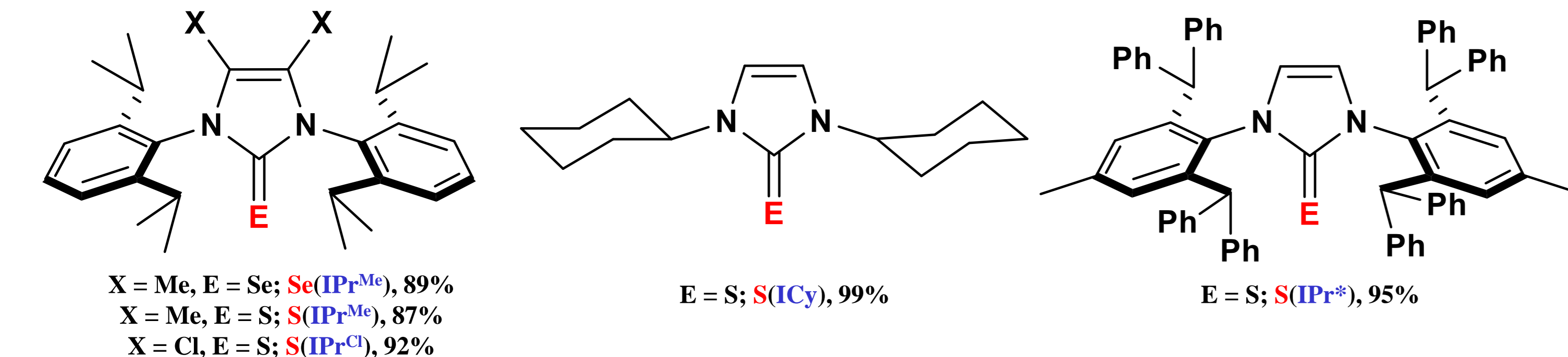
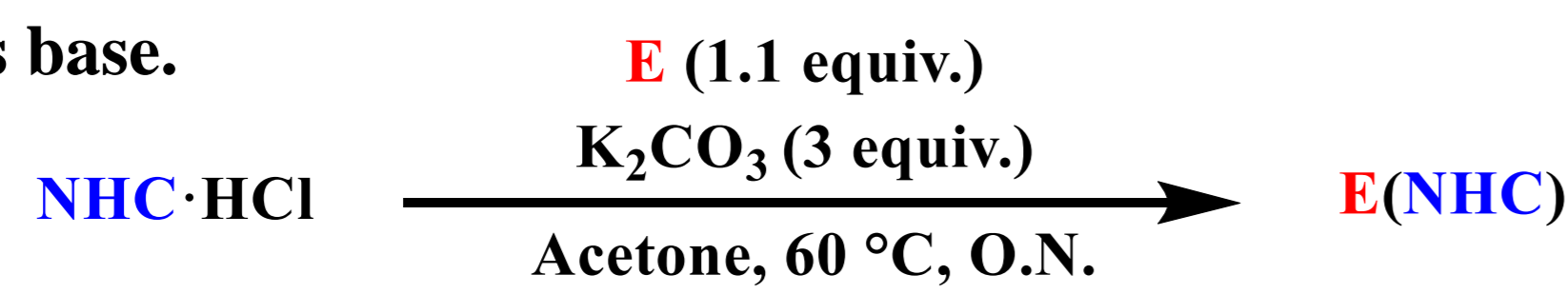
INTRODUCTION

Over the last decade, NHCs (N-heterocyclic carbenes) have attracted significant attention from the organic and inorganic scientific communities due to their unique structural properties and reactivity. Chalcogen-based NHC derivatives have recently been investigated for their potential to probe the electronic and steric properties of NHCs as well as their interesting coordination chemistry to transition metals.[1-4] Selenium NMR spectroscopy has been used to investigate the π -accepting ability of various NHCs as well as the behavior of that ability when coordinated to transition metals (e.g., Cu, Ag and Au). In addition, the crystallisation pattern (monomer, dimer and rearranged structures) of these Se(NHCs), when coordinated to the aforementioned transition metals, offers additional information on their electronic and steric properties. We also believe that understanding all of these patterns may help us establishing a clear trend that can be highly useful in coordination chemistry as well as in biomedical applications.

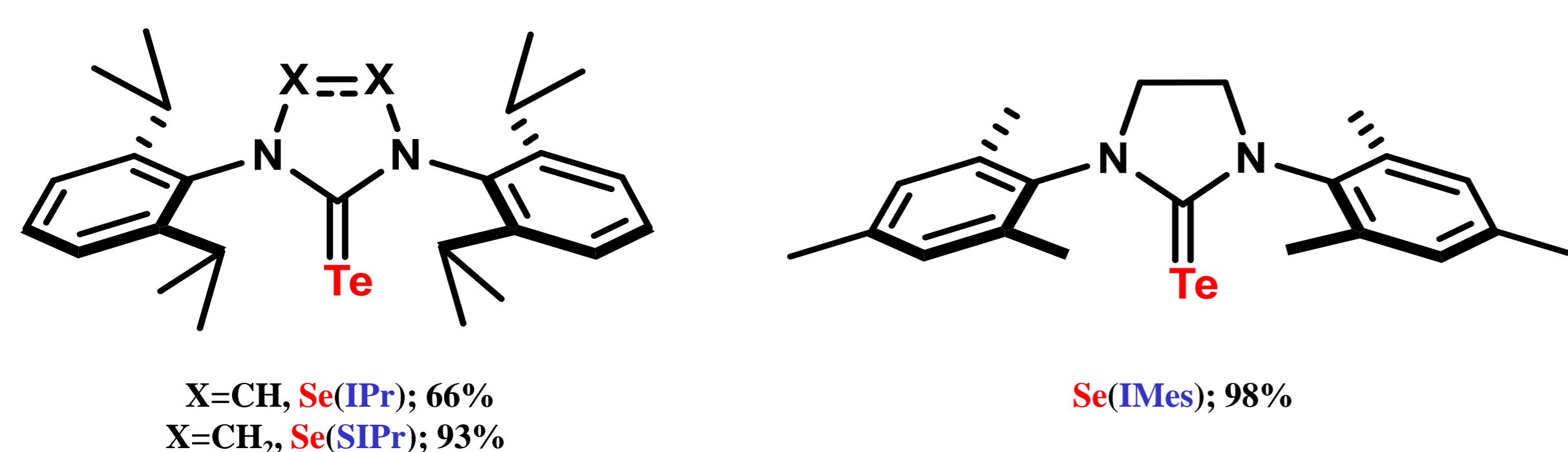
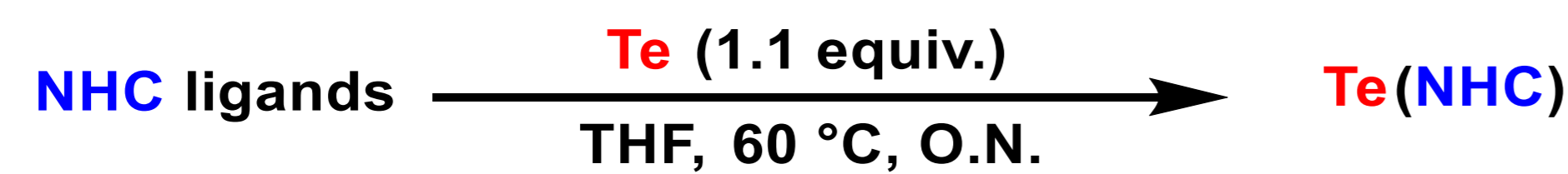
Herein, we focus on continuing our previous work on selenoureas and on extending this research to thio- and telloureas by investigating new synthetic routes and studying their coordination patterns to transition metals as well as revealing the structures geometries of these complexes after oxidizing with halogens.

I. SYNTHESIS

- Selenourea and thiourea compounds were synthesised via deprotonation of various imidazolium salts, using K_2CO_3 as base.

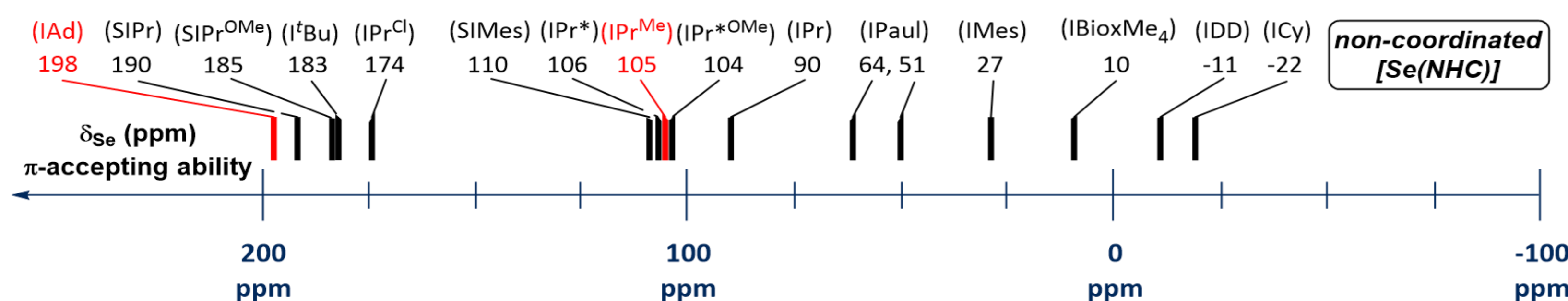


- Tellourea compounds were synthesised using a different strategy starting from free NHC ligands.



III. CHEMICAL SHIFTS OF SELENOUREA NHCs AND THEIR METAL COMPLEXES

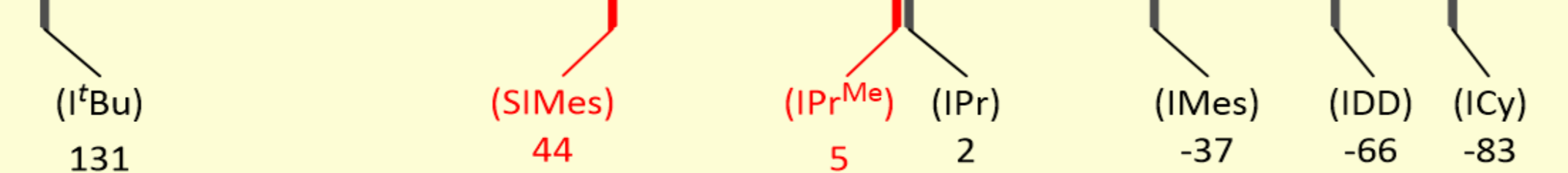
This figure shows the ⁷⁷Se chemical shifts and the relative π -accepting ability (increases from right to left) for several selenourea compounds made in this work (red) and for the ones made in our previous work [1-2].



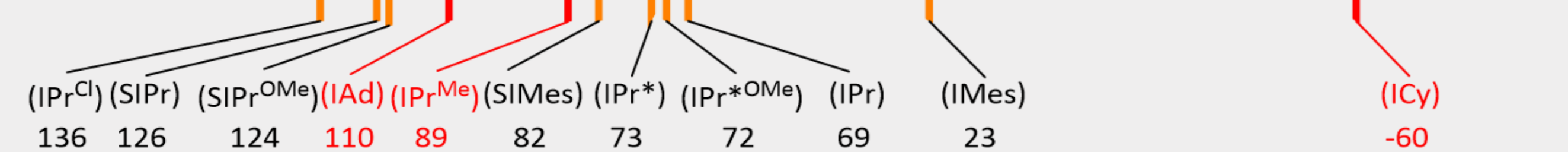
Cu-coordinated [Se(NHC)]



Ag-coordinated [Se(NHC)]



Au-coordinated [Se(NHC)]



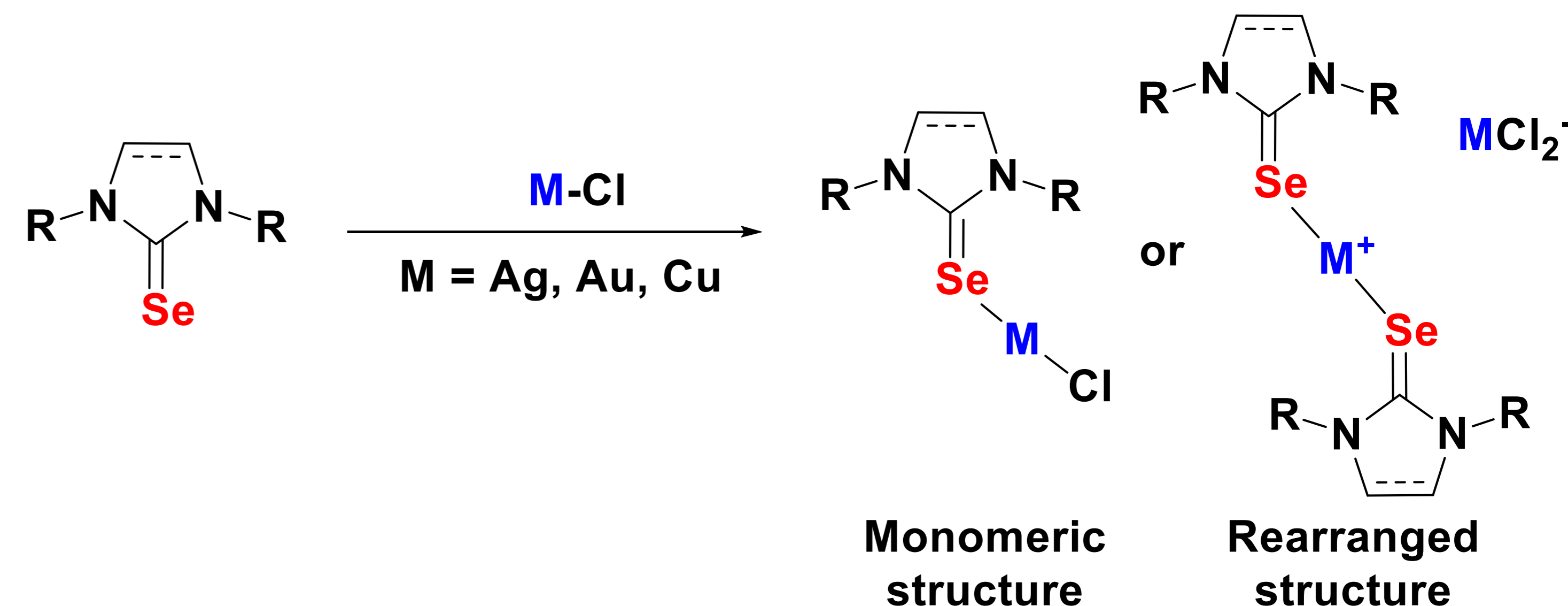
SUMMARY

- Synthesis of selenourea and thiourea compounds from NHC salts.
- Synthesis of tellourea compounds from free NHC ligands.
- Coordination of Se(NHCs) to gold, silver and copper chloride.
- Bromination of seleno- and thio-urea NHCs.
- All the complexes were characterized by ¹H, ¹³C and Se NMR spectroscopy as well as elemental analysis.
- Several examples were characterized and studied by X-ray crystallography. These complexes can be highly influenced by the NHC/metal combination.

We greatly appreciate the support of Ghent University.

- [1] Marina Saab, David J. Nelson, Nikolaos V. Tzouras, Tahani A. C. A. Bayrakdar, Steven P. Nolan, Fady Nahra and Kristof Van Hecke *Dalton Trans.*, 2020,49, 12068-12081
- [2] F. Nahra, K. Van Hecke, R. Kennedy and D. J. Nelson, *Dalton Trans.* 47(2018) 10671-10684.
- [3] D. J. Nelson, F. Nahra, S. R. Patrick, D. B. Cordes, A. M. Z. Slawin, and S. P. Nolan, *Organometallics*. 33(2014) 3640-3645.
- [4] D. J. Nelson, A. Collado, S. Manzini, S. Meiries, A. M. Z. Slawin, D. B. Cordes, and S. P. Nolan, *Organometallics*. 33(2014) 2048-2058.

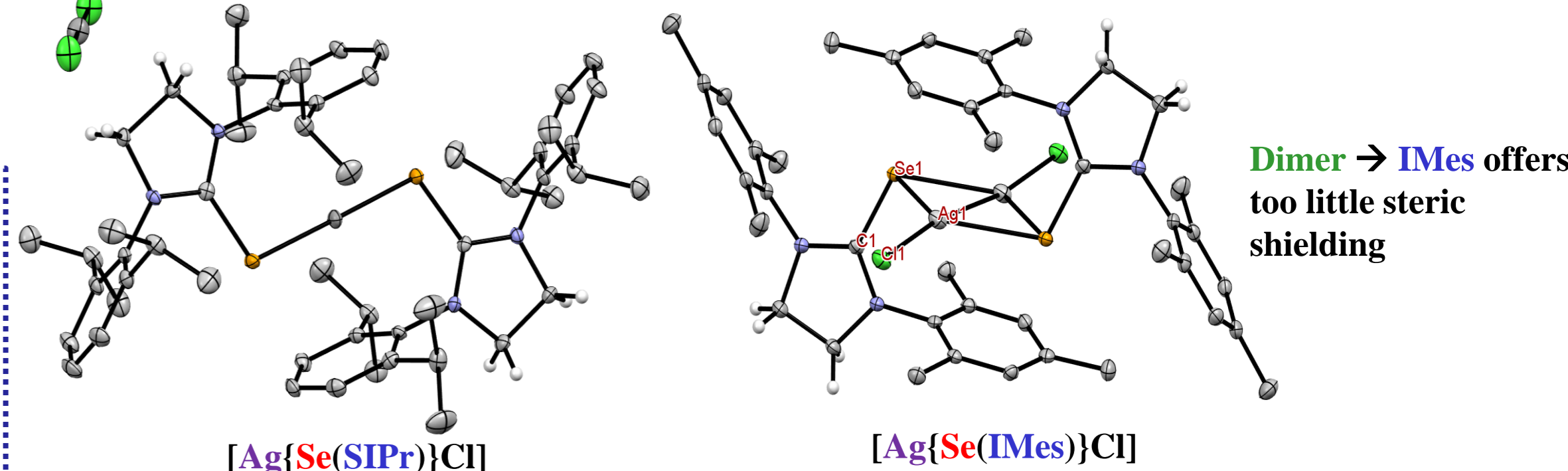
II. COORDINATION OF TRANSITION METALS TO SELENOUREAS



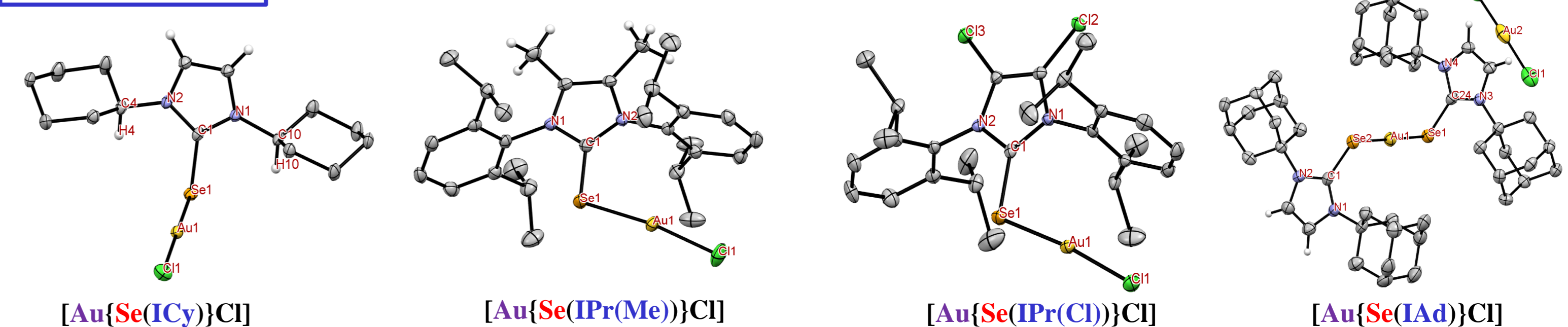
Silver complexes

Rearranged Structure \rightarrow SIPr exhibits high π -accepting ability

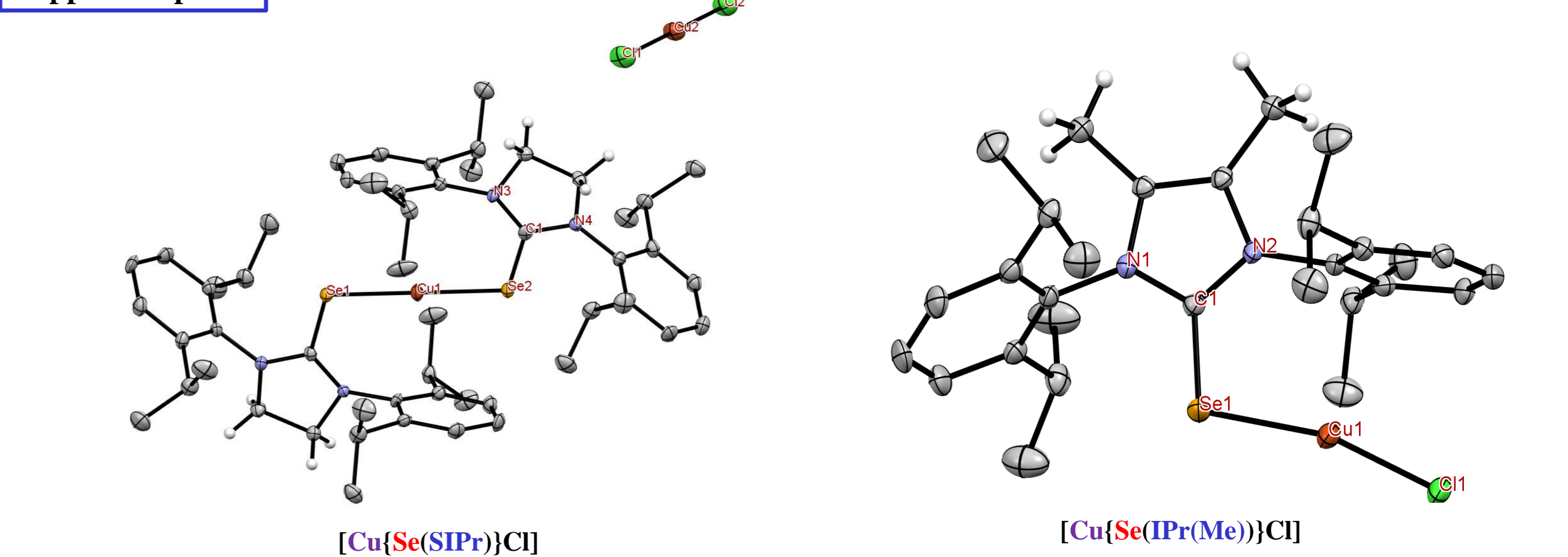
In comparison with our previous work,[1-2] [Ag{Se(IPr)}Cl] led to the observation of monomeric crystals under the same conditions. This implies that IPr offers high steric shielding and low π -accepting ability.



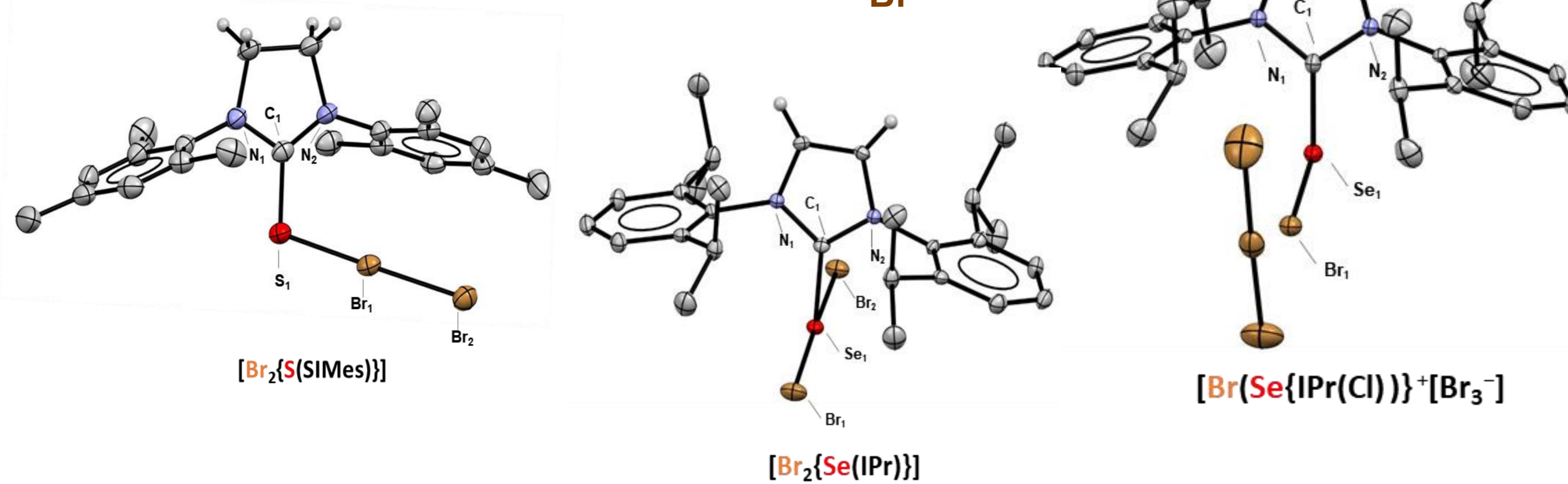
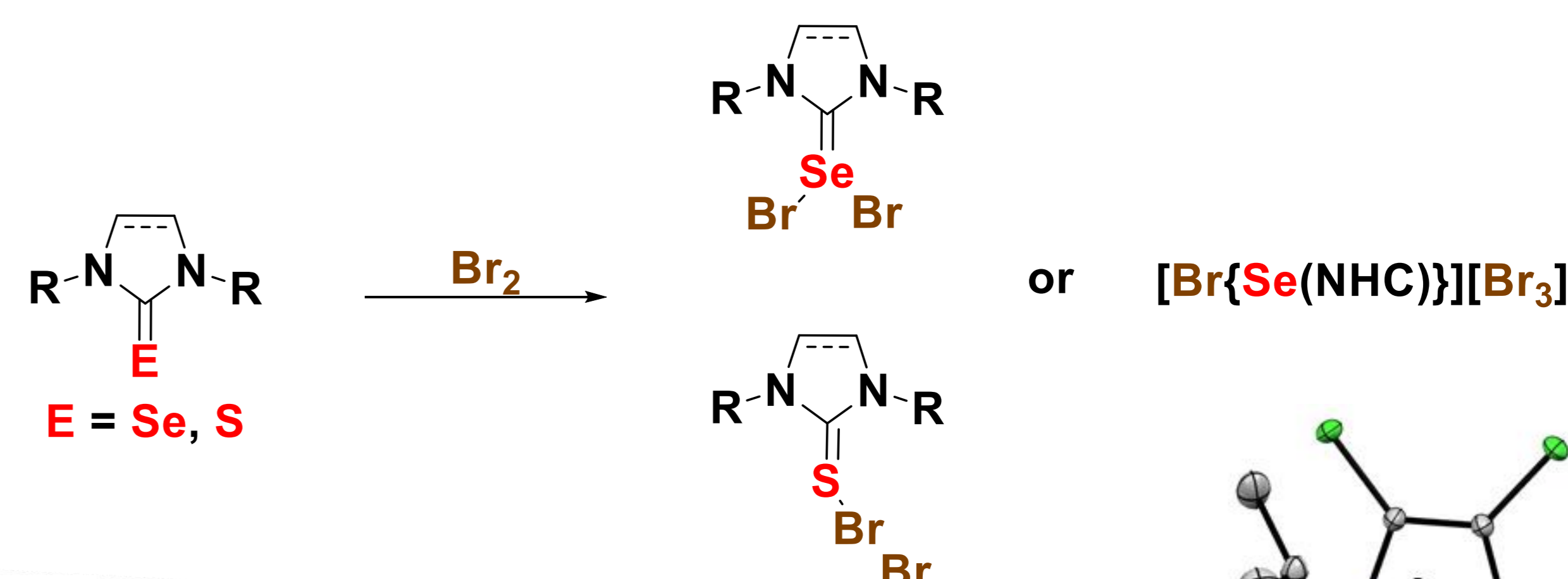
Gold complexes



Copper complexes



IV. BROMINATION OF SELENO- AND THIO-UREA NHCs



The geometry of these products are highly affected by:

- Nature of the donor (chalcogen)
- Type of the halogen or inter-halogen
- Stoichiometry of the reaction
- Type of the ligand bound to the chalcogen

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