

SILVER AND RUTHENIUM COMPLEXES IN MOLECULAR CHEMISTRY: TOWARDS GREEN CHEMISTRY AND SUSTAINABLE DEVELOPMENT

Keyu Mao¹, Romain Melot¹, Sophie Poulain-Martini¹, Véronique Michelet¹

¹Université Côte d'Azur, Institut de Chimie de Nice, Parc Valrose, 06108, Nice Cedex 2, France.

In the context of the key principles of Green Chemistry,¹ the development of efficient, clean and mild strategies to access cyclized and functionalized molecules is highly important in the field of organic chemistry. We became interested in the reactivity of enynes in the presence of silver and ruthenium complexes. We investigate the cyclization of functionalized 1,6-enynes and showed that silver hexafluoroantimonate² catalyzed the intramolecular [4+2] cycloaddition reaction of amide-1,6-enynes, providing tricyclic and tetracyclic compounds. The effects of different catalysts (silver salts, gold and platinum complexes) on this reaction were also investigated, leading to a series of cyclic amides obtained in good yields.³ In parallel, we developed a ruthenium-mediated ring-closing enyne metathesis transformation of alkynyl B-anthranilamide (B(aam)) to prepare functionalized polycyclic azaborine skeletons. B(aam)-tethered enynes reacted with with Grubbs catalyst, affording the corresponding *exo*-cyclic compounds in good yields (25 examples, yields up to 89%).⁵ This methodology was optimized and performed in dimethyl carbonate⁶ as a green solvent, providing a direct and environmentally friendly access to functionalized azaborine scaffolds.



Figure 1: Silver and ruthenium-catalyzed cycloisomerization reaction of nitrogenated enynes

Reference(s)

¹ Anastas, P. T.; Warner, J. C. Oxford university press, **2000**.

² Plevová, K.; Prieto, Pabon L. J.; Gaysinski, M.; Poulain-Martini, S.; Michelet, V. ChemPlusChem, 2022, 87, e202200217. Chen, X.; Fontaine-Vive, F.; Poulain-Martini, S.; Michelet, V. Catal. Commun. 2020, 147, 106117.
³ Mao, K.; Plevová, K.; Chen, X.; Prieto, Pabon L. J.; Poulain-Martini, S.; Michelet, V. C. R. Acad. Sci. (Special)

³ Mao, K.; Plevová, K.; Chen, X.; Prieto, Pabon L. J.; Poulain-Martini, S.; Michelet, V. *C. R. Acad. Sci.* (Special issue: Chemist Women in France), **2025**, *in press*.

⁴ Micalizio, G. C.; Schreiber, S. L. Angew. Chem. Int. Ed. 2002, 41, 152. Micalizio, G. C.; Schreiber, S. L. Angew. Chem. Int. Ed. 2002, 41, 3272. Renaud, J.; Graf, C. D.; Oberer, L. Angew. Chem. Int. Ed. 2000, 112, 3231.
⁵ Mao, K.; Melot, R.; Michelet, V. Org. Lett. 2025, under revision.

⁶ Miao, X.; Fischmeister, C.; Bruneau, C.; Dixneuf, H. ChemSusChem, 2008, 1, 813. Fiorani, G.; Perosa, A.; Selva, M. *Green Chem.*, **2018**, *20*, 288.

.....