

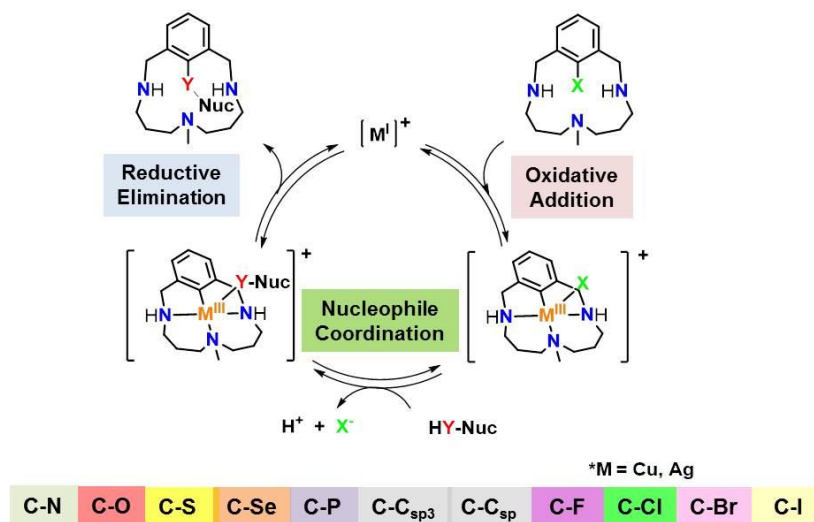
# Aryl halide macrocyclic model substrates for mechanism elucidation of coinage metal-catalysed cross-coupling reactions

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Cross-coupling catalysis has been a breakthrough for organic synthesis providing chemists with new approaches to build up complex molecules since its blooming in the early seventies. Although in the early reports of methodologies relying in cross-coupling reactions the catalyst was invariably palladium-based, soon they were extended to a much broader range of transition metals including coinage metals. Distinct from palladium catalysis, that holds a well-established mechanistic basis, the mechanistic understanding of coinage metal cross-coupling reactions is much more limited.<sup>[1]</sup>

Herein we show direct experimental observation of the implication of aryl-M(III) (M = Cu, Ag) species as the key intermediate species of a model C-Nucleophile bond forming cross-coupling reactions. This results demonstrate the plausibility that group 11 transition metal-catalysed cross-coupling reactions operate through M(I)/M(III) redox catalytic cycles involving oxidative addition and reductive elimination fundamental steps with a wide range of nucleophiles of different nature.<sup>[2]</sup>



## References:

- [1] Casitas, A.; Ribas, X, *Chem. Sci.*, **2013**, *4*, 2301-2318.  
[2] a) Font, M.; Parella, T.; Costas, M. and Ribas, X. *Organometallics*. **2012**, *31*, 7976-7982. b) Rovira, M.; Font, M. and Ribas, X. *ChemCatChem*. **2013**, *5*, 687-691. c) Rovira, M.; Font, M.; Acuña-Parés, F.; Parella, T.; Luis, J. M.; Lloret-Fillol, J. and Ribas, X. *Chem. Eur. J.* **2014**, DOI: 10.1002/chem.201402711. Font, M.; Acuña-Parés, F.; Parella, T.; Serra, J.; Luis, J. M.; Lloret-Fillol, J.; Costas, M.; Ribas, X. *Nat. Commun.*, *Accepted*.