COBALTACYCLES FOR C-H BOND ACTIVATION UNDER OXIDATIVE CONDITIONS

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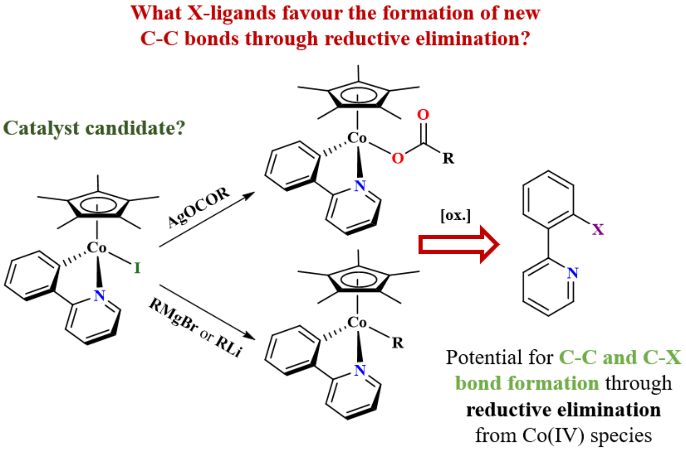

What X-ligands favour the formation of new C-C bonds through reductive elimination?

Catalyst candidate?

Potential for **C-C and C-X bond formation** through **reductive elimination** from Co(IV) species

Historically dominated by precious and rare metal catalysts, the field of C-H bond functionalisation has recently been subject to a rise in interest for the use of the more readily available 3d row metal as alternatives. Among these, cobalt metallacycles are very powerful candidates, especially due to the interesting parallels that can be drawn from the chemistry of iridium and rhodium, all while providing valuable insights into the chemistry of other 3d row metals. Still, the unique set of properties and reactivity of these cobalt-base complexes, along with unknown reaction mechanisms, pose an important challenge. One example of this is the surprising discovery that they transform into catalytically active nanoparticles in the presence of hydride sources, capable of hydrosilylating aromatic carbonyls and nitriles, which is not observed for the iridium equivalent.[1] It is therefore crucial to carry out in-depth studies of the behaviour of these Co-complexes under different conditions. Remarkably, once oxidised to the Co(IV) species, CoCp*(2-*phpy*)X (Cp*: 1,2,3,4,5-pentamethylcyclopentadienyl, 2-*phpy*: 2-phenylenepyridinyl) complexes show capricious behaviours depending on the nature of the X-ligand (halide, carboxylate, alkyl, aryl, etc.). Thus, a small library of new cobaltacycles was synthesised by varying the X-ligand, using known and new reaction pathways, notably involving organolithium and Grignard reagents or silver salts. Three main pathways are observed experimentally after oxidation: (i) the reductive elimination of functionalized 2-phenylpyridine (2-*phpy*-X), (ii) the cyclocondensation of the non-innocent Cp* ligand with the 2-*phpy* ligand or (iii) the decomposition by 2-*phpy*-H hydrodemetalation.[2] The question that arises is how to predict the reactivity in order to design a system capable of achieving the formation of new C-C bonds: the innovative approach of using the independent gradient model/intrinsic bond strength index (IGM/IBSI) method as a predictive tool was introduced, locally evaluating non-covalent interactions between reactive centres of the complex as a function of the X ligand, successfully and reliably predicting the experimental reaction outcomes.[2]

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[1] Antuña-Hörlein, C.; Wu, F.; Deraedt, C.; Bouillet, C.; Djukic, J.-P., *Eur. J. Inorg. Chem.*, **2023**, *26*, e202200563, *in press.* DOI: 10.1002/ejic.202200563

[2] Loir-Mongazon, L.; Antuña-Hörlein, C.; Deraedt, C.; Cornaton, Y.; Djukic, J.-P. Synlett, **2022**, *33*, *in press.* DOI: 10.1055/a-1937-9296