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Structural and electronic characterization of the principal catalytic components in C-H bond functionalization by triazamacrocyclic-Cu complexes

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Herein, the electronic and geometric structure of first row transition metal mediated C-H bond activation and C-X cross-coupling reactions, was directly probed using X-ray absorption spectroscopy. The experimental data was correlated with theoretical calculations in the hopes of better understanding the principal catalytic species, reactive intermediates, and their structure-function relationship.

The study focuses on a series of aryl-Cu complexes based on a triazamacrocyclic ligand scaffold. Chelation of Cu(II) by the arene ligand is followed by PCET C-H bond activation, yielding an aryl-Cu(III) and aryl-Cu(I) species via a disproportionation reaction. The aryl-Cu(III) species facilitates C-Y heteroatom cross-coupling reactions (Y=N, O, S, Se) and represents the first direct evidence for an organo-Cu(III) intermediate in copper-catalyzed oxidative coupling. The initial arene-Cu(II) complex is proposed to form a three center three electron interaction prior to C-H activation but has not been structurally characterized. Therefore XANES and EXAFS analysis was employed to elucidate the electronic and geometric structure at the copper center of the principal catalytic components. Furthermore, the impact of the metal center was explored by also characterizing the analogous aryl-Ni(II) complex. In the case of nickel the initial arene-metal complex is proposed to form a classical three-center, two-electron agostic interaction, and unlike the copper system, C-H activation proceeds without metal oxidation.

Ultimately understanding these systems will lead to more economic, sustainable and environmentally benign synthetic pathways with important applications in pharmaceuticals and agrochemicals. Current approaches to C-H bond functionalization involve either harsh reaction conditions that do not allow the selective transformations desired in organic synthesis, or use heavy metals that are scarce, expensive and form toxic byproducts. Therefore the use of abundant, non-toxic and economically sustainable first row transition metals is an attractive alternative.

References

(1) Ribas, X.; Calle, C.; Poater, A.et al. Journal of the American Chemical Society 2010, 132, 12299.

(2) Casitas, A.; Canta, M.; Sola, M.et al. Journal of the American Chemical Society 2011, 133, 19386.

(3) Casitas, A.; Ioannidis, N.; Mitrikas, G.et al. Dalton Transactions 2011, 40, 8796.

(4)Casitas, A.; King, A. E.; Parella, T.et al. Chemical Science 2010, 1, 326.

(5) Casitas, A.; Ribas, X. Chemical Science 2013, 4, 2301.

(6) Ribas, X.; Xifra, R.; Parella, T.et al. Angewandte Chemie-International Edition 2006, 45, 2941.

(7) Ribas, X.; Jackson, D. A.; Donnadieu, B.et al. Angewandte Chemie-International Edition 2002, 41, 2991.

Caption (s) - Add figures as attached files (2 fig. max)

Coupling of X-ray absorption experimental data with theoretical calculations to elucidate the principal species in C-H activation by triazamacrocyclic-copper complexes.

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