

In my Element: Copper

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Dedicated to my mentors Ernesto Carmona and Maurice Brookhart

After working with molybdenum, tungsten, ruthenium and iridium during my Ph. D. studies, and the initial part of my postdoctoral studies, I could not imagine that copper would change my scientific life. It was after an impressive lecture by David Evans as part of the seminar program of the Department of Chemistry at UNC-Chapel Hill that I felt attracted by this metal and its capabilities to catalyze carbene and nitrene transfer reactions. After that lecture, and a brief talk with my supervisor, I focused in complex $\text{Tp}^*\text{Cu}(\text{C}_2\text{H}_4)$, previously described by Ibers, as a potential catalyst for those transformations, an election based on my knowledge about trispyrazolylborate ligands from my earlier work with iridium and tungsten. I found a quite remarkable catalytic behavior of $\text{Tp}^*\text{Cu}(\text{C}_2\text{H}_4)$ for effective olefin cyclopropanation and aziridination and alkyne cyclopropanation, a discovery that opened, for me, the door toward copper chemistry.

Moving to the Universidad de Huelva in 1993 gave me the opportunity to develop my own research, which I initially decided to be based on the functionalization of hydrocarbons by carbene, nitrene or oxo moieties using Tp^*Cu catalysts. After several initial findings, we started a collaboration with Jerry Trofimenko in 2000, testing some old as well as also novel Tp^* ligands with copper in several organic reactions. At that time, we found highly selective catalysts for the preferential formation of

cis-cyclopropanes or the direct functionalization of $\text{C}_{\text{sp}^2}\text{-H}$ and $\text{C}_{\text{sp}^3}\text{-H}$ by carbene and/or nitrene insertion reactions. From these systems we gained knowledge to design more active or selective catalysts in subsequent transformations along the years. For example, using ethyl diazoacetate as the carbene source, an array of substrates from methane to polyolefins were functionalized, with the appropriate tuning of the ligands, whereas the oxidation of $\text{C}_{\text{sp}^2}\text{-H}$ and $\text{C}_{\text{sp}^3}\text{-H}$ bonds was also achieved with hydrogen peroxide as the oxidant. Copper has also led to the discovery of some novel transformations in our laboratory, in all cases involving copper-nitrene intermediates. It is the case of the conversion of furanes into dihydropyridines, alkynes into sulfonamides or amines into aminimides. The direct formation of oxazoles from alkynes and carbonyl azides was also discovered with a copper catalyst.

Gratifyingly, copper has not only occupied the center of my *academic* research in the last two decades but has also provided a very enjoyable relationship with an industrial partner, a copper smelter nearby our University. We have the opportunity of contributing to some projects regarding copper production, from a purely inorganic chemistry point of view, in line my academic teaching duties.

Looking back to all those achievements promoted by this metal, there is no doubt that copper finds a special place in my scientific heart.

Table 1. Author Profile

Position	Professor of Inorganic Chemistry
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Homepage	http://www.uhu.es/ciqso/catalisis-homogenea.html
Education	Chemistry Degree, University of Sevilla, Spain, 1987 .Ph.D. September 1991, Professor Ernesto Carmona, supervisor. Postdoctoral work: Oct 1991-Feb 1993, Prof. Maurice Brookhart, University of North Carolina, Chapel Hill (NC). Jun-Sep 1994, Visiting scientist: Dupont Experimental Station, Wilmington, Delaware, Dr. Emilio Bunel.
Awards & Recognitions	Research Prize and Gold Medal (2016), Homogeneous Catalysis Award of the Royal Society of Chemistry (2015), Inorganic Chemistry Award of the Spanish Royal Society of Chemistry (2007). Member of the Academia Europaea (2018), and of the Royal Spanish Academy of Sciences (Corresponding, 2014). FRSC (2014).
Research interests	Development of medium- and late transition-metal complexes as catalysts for transformations involving hydrocarbons, particularly those bearing non-activated C-H bonds.
Hobbies	Collecting stamps, playing (bad) golf.



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