## Exploring bonding situation and reactivity of halogenated derivatives. The role of computational chemistry in the understanding of these new systems.

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Computational chemistry is now an integral part of nearly every branch of chemistry and has become indispensable for understanding the mechanisms behind chemical reactions. The combined experimental and theoretical approach is increasingly important in addressing a wide range of organometallic challenges, offering a deeper insight into reactivity through this collaborative synergy. By examining electronic structures, new bonding situations and reaction pathways, while carefully analyzing the contributing factors (such as electrostatic or orbital interactions and steric repulsion), important mechanistic information is uncovered, as well as valuable insights into the stabilization of novel systems.

In the past few years in collaboration with experimenters, we have focused on the reactivity of different types of halogen-containing derivatives. The fruitful interplay between theory (DFT, reactivity tools) and experiment has been highlighted through a range of examples. The contribution of computational chemistry has been emphasized, particularly in describing the electronic structure, the bonding situation and the reaction mechanisms. In this presentation, some of these examples will be discussed. In collaboration with the team of Y. Landais and D. Taton (ISM & LCPO, Bordeaux), we studied singlet acyclic amino(haloaryl)carbenes. The role of the halogen (Br, Cl, F) on their thermodynamic stability was investigated both experimentally and theoretically.<sup>[1]</sup> With the aim to open new avenues in gold chemistry, in collaboration with the team of D. Bourissou (LHFA, Toulouse), we were interested in highlighting new reactivity and new bonding situations. We explored in depth the structures and reactivity of electrophilic difluorocarbene-gold complexes by combining experimental studies, DFT calculations, NBO and EDA analyses.<sup>[2]</sup> Pivotal transformations such as challenging Csp<sup>3</sup>-Csp<sup>3</sup> reductive elimination, were also studied and made possible with this metal and the use of a (P,B) ambiphilic ligand, through a zwitterionic path involving a B $\leftarrow$ Cl $\rightarrow$ Au key intermediate. <sup>[3]</sup> Finally, with the team of V. Bizet and N. Blanchard (LIMA, Strasbourg), we described the reactivity of SF<sub>5</sub>-alkynes with N-nucleophile, leading to a single regio- and stereoisomer (β-regioselectivity). Experimental and computational comparative studies between SF<sub>5</sub>- and CF<sub>3</sub>-alkynes have been performed to explain the difference of reactivity and selectivity observed between these two fluorinated motifs.<sup>[4]</sup>



[1] Magis, D.; Cabrera-Trujillo, J-J.; Vignolle, J.; Sotiropoulos, J-M.; Taton, D.; Miqueu, K.; Landais, Y., J. Am. Chem. Soc., 2024, 146, 16802.

[2] a) unpublished results. b) For other ex., see : Rigoulet, M.; Vesseur, D.; Miqueu, K.; Bourissou, D., *ACIE*, **2022**, *61*, e202204718.
[3] Theulier, C. A.; Garcia-Rodeja, Y.; Miqueu, K.; Bouhadir, G.; Bourissou, D., *J. Am. Chem. Soc.* **2023**, *145*, 10800.
[4] Popek, L.; Cabrera-Trujillo, J- J.; Debrauwer, V.; Blanchard, N.; Miqueu, K.; Bizet, V. *ACIE*, **2023**, *62*, e202300685.

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