## Vinyl cation Intermediates Tamed by Weakly Coordinating Anions: From Mechanistic Curiosity to Synthetic Tools



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Vinyl cations, long overlooked due to their supposed uncontrollable nature, have recently become the focus of renewed research into their physical and chemical properties. This has led to exciting new applications in homogeneous catalysis. The Mayr group has played a pivotal role in dispelling the myths surrounding these intermediates, revealing that their stability is comparable to that of tertiary carbocations. Nevertheless, due to the substantial energy barrier associated with sp«sp² rehybridization, vinyl cations tend to be sluggish electrophiles.



Building on this breakthrough, several research groups have addressed this electrophilicity issue and have successfully harnessed vinyl cations to develop novel reactions. Our group, in particular, has devised a gentle and effective method for the bimolecular vinylation of arenes. This involves employing a lithium salt as a catalyst to activate vinyl triflates and facilitate the formation of a vinyl carbocation. Furthermore, we have extended this strategy to conduct substitution reactions between vinyl cations and various nucleophiles, both in inter- and intramolecular settings.

## References:

- 1. Aluminum-Catalyzed Intramolecular Vinylation of Arenes by Vinyl Cations. Lin, W; Alix, A.; Guillot, R.; Gandon, V.\*; Bour, C.\*, Org. Lett., 2024, 26, 3267
- Squaramide/Li\*-Catalyzed Direct S<sub>N</sub>1-Type Reaction of Vinyl Triflates with Difluoroenoxysilanes through Vinyl Cations Chen. Y.; Gandon, V.\* Bour, C.\*; Org. Lett., 2022, 24, 6978.
- 3. Potassium Carbonate to Unlock a GaCl3-Catalyzed C-H Propargylation of Arenes. <u>Vayer, M.; Rodrigues, S.; Miaskiewicz, S.;</u> Gatineau, D.; Gimbert, Y.; Gandon, V.\*; **Bour, C.** \*ACS Catal., **2022**, *12*, 305.
- 4. Bimolecular vinylation of arenes by vinyl cations. Li, Z.; Gandon, V.; Bour, C. Chem. Commun. 2020, 56, 6507.
- 5. Synthesis of Medium-Sized Carbocycles by Gallium-Catalyzed Tandem Carbonyl-Olefin Metathesis/Transfer Hydrogenation. Djurovic, A.; Vayer, M.; Li, Z.; Guillot, R.; Baltaze, J.-P.; Gandon, V.; **Bour, C.\*** Org. Lett. **2019**, *21*, 8132.
- Iron-Catalyzed Reductive Ethylation of Imines Using Ethanol. Vayer, M.; Morcillo, S.; Dupont, J.; Gandon, V.; Bour, C.\*
  Angew. Chem. Int. Ed. 2018, 57, 3228.

Prof. Christophe Bour was born in Strasbourg, France, where he began his studies in chemistry. He earned his PhD in Organic Chemistry from the University of Strasbourg in 2006 under the supervision of Professor Jean Suffert, working on synthetic methodologies involving transition metal catalysis and reactive intermediates. Following his doctoral studies, he joined the group of Professor Antonio M. Echavarren at the Institute of Chemical Research of Catalonia (ICIQ) in Tarragona, Spain, as a postdoctoral researcher. There, he contributed to the development of gold-catalyzed transformations and explored the reactivity of complex polyunsaturated substrates.

In 2010, Christophe Bour was appointed Assistant Professor at the University Paris-Saclay (ICMMO – Institut de Chimie Moléculaire et des Matériaux d'Orsay). He was promoted to Lecturer (Maître de Conférences) in 2015 and achieved the rank of Full Professor in 2024.

His research lies at the interface of organic synthesis, catalysis, and reaction mechanism, with a particular emphasis on the design of new electrophilic activation modes, including the generation and application of high-energy intermediates such as vinyl cations and carbocations in stereoselective and cascade processes. He has made contributions to the use of weakly coordinating anions and superacid-based catalysis to unlock unconventional reactivity patterns, with applications in the synthesis of bioactive scaffolds and structurally complex molecules.

