

The Renewed Interest in Vinyl Cations as Reactive Intermediates

Christophe BOUR

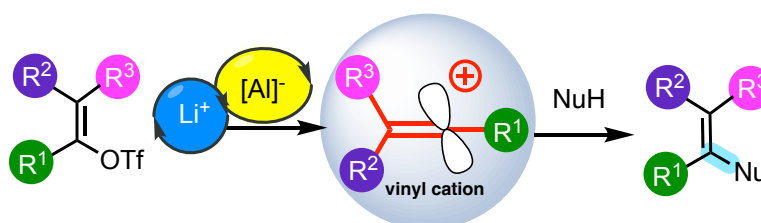
Institut de Chimie Moléculaire et des Matériaux d'Orsay
Université Paris-Saclay, Bâtiment Henry Moissan

université
PARIS-SACLAY

christophe.bour@universite-paris-saclay.fr



Vinyl cations, long overlooked due to their supposed uncontrollable nature, have recently become the focus of renewed research into their physical and chemical properties.¹ 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 actually comparable to that of tertiary carbocations.² Nevertheless, due to the substantial energy barrier associated with $sp \leftarrow sp^2$ 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.³ 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.⁴

¹Niggemann, M.; Gao, S. *Angew. Chem. Int. Ed.* **2018**, *57*, 16942

²Byrne, P. A.; Kobayashi, S.; Würthwein, E.-U.; Ammer, J.; Mayr, H. J. *Am. Chem. Soc.* **2017**, *139*, 1499

³Li, Z.; Gandon, V.; Bour, C. *Chem. Commun.* **2020**, *56*, 6507

⁴Chen, Y.; Gandon, V.; Bour, C. *Org. Lett.* **2022**, *24*, 6978