M2 Internship 2022-2023

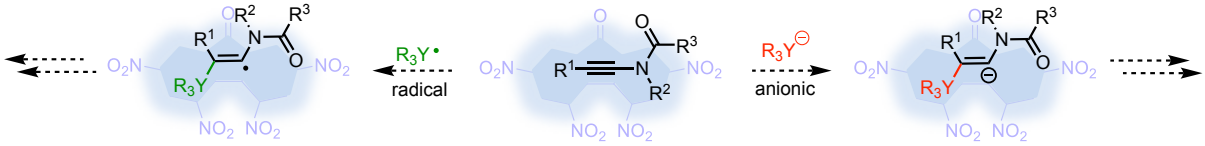
Organic Charge Transfer Complexes for Catalysis

Project description:

Charge transfer complexes (CTCs) have been extensively studied in materials science owing to their inherent properties in the fields of charge transport, light emission, nonlinear optics and external stimuli responsiveness.[1] Their π-acid component are UV absorbers and their color changes upon contact with π or Lewis bases provide evidence for CTC formation.[2]

While the propensity of CTCs to absorb light has been advantageously and massively used to excite molecules and trigger reactivity,[3] in sharp contrast, **the use of the π-acidity to stabilize anions or activate electron-rich molecules in the context of catalysis has hardly been studied**.

In order to probe more generally the catalytic ability of CTCs, we settled on the study of the activation of electron-rich nitrogen. Thus, by forming a CTC with HMDS, we successfully withdrew electron density from the nitrogen, and ultimately, weakened the N–Si bond.[4] On reaction with alcohols, this promotes the transfer of the trimethylsilyl group to the oxygen atom.[5] Next, we would like to tackle the activation of electron-rich ynamides. More precisely, element–metal addition reactions with organometallic reagents (either through radical or anionic processes) will be studied.



Y = C, Si, Ge

This project comprises the synthesis of the π-acid catalysts, i.e. electron deficient arenes. Next, their ability to form CTC with ynamides will be assessed by UV-vis measurements while their reactivity will be probed. **As such, we intend to revisit the methodologies of element–metal addition reactions developed in our group[6] with this new supramolecular mode of activation.**

Location: Sorbonne Université, IPCM, ROCS team, 4 place Jussieu, Paris, France

Period: from February to mid-July 2023 (5 months)

Gratification: https://www.service-public.fr/simulateur/calcul/gratification-stagiaire

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[1] W. Wang, L. Luo, P. Sheng, J. Zhang, Q. Zhang, *Chem. Eur. J.* **2020**, *27*, 464.

[2] Sulzberg and Cotter US patent 3637798 25 (**1972**).

[3] G. E. M. Cristenza, D. Mazzarella, P. Melchiorre, *J. Am. Chem. Soc.* **2020**, *142*, 5461.

[4] Manuscript in preparation

[5] M. A. Ashraf, Z. Liu, C. Li, D. Zhang, *Appl Organomet Chem.* **2021**, *35*, e6131; A. V. Narsaiah, *J. Organomet. Chem.* **2007**, *692*, 3614.

[6] K. de la Vega-Hernández, E. Romain, A. Coffinet, K. Bijouard, G. Gontard, F. Chemla, F. Ferreira, O. Jackowski, A. Perez-Luna A. *J. Am. Chem. Soc.* **2018**, *140*, 17632 ; C. Fopp, E. Romain, K. Isaac, F. Chemla, F. Ferreira, O. Jackowski, M. Oestreich, et A. Perez-Luna *Org. Lett.* **2016**, *18*, 2054 ; E. Romain, C. Fopp, F. Chemla, F. Ferreira, O. Jackowski, M. Oestreich, A. Perez-Luna *Angew. Chem. Int. Ed.*, **2014**, *53*, 11333.