

# Unusual Redox Cycles for Aromatic Trifluoromethylation through High Oxidation State Organometallics

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# Unusual Redox Cycles for Aromatic Trifluoromethylation through High Oxidation State Organometallics

Noel Nebra\*

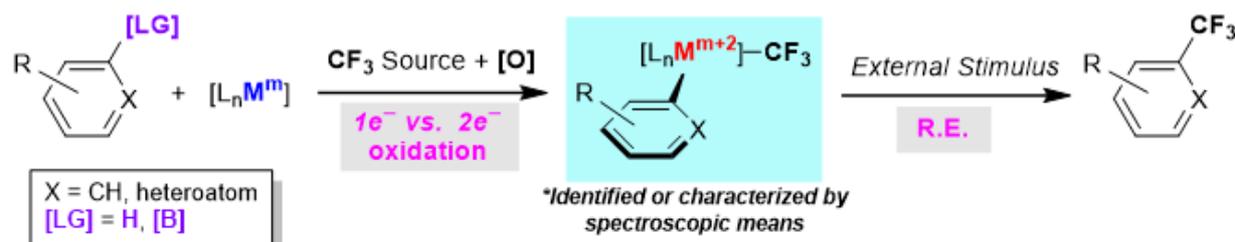
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Fluorine atoms drastically affect the biological properties of organic synthons.<sup>[1]</sup> Among the most common perfluorinated groups, the CF<sub>3</sub> moiety occupies a preferential place in drug discovery and agrochemical design. Creating C–CF<sub>3</sub> bonds *via* cross-coupling reactions is an appealing strategy to build molecular complexity. However, unfortunately, the aryl–CF<sub>3</sub> bond formation *via* reductive elimination (R.E.) from [aryl–M–CF<sub>3</sub>] fragments represents a challenging task. An original approach to favor the key R.E.

step resides in the preparation of high-valent organometallics. In this seminar, the utility of high oxidation state MCF<sub>3</sub> compounds to enable the trifluoromethylation of different aromatic scaffolds will be disseminated (**Figure 1**). In particular, significant advances on the synthesis and characterization of Ni<sup>IV</sup>CF<sub>3</sub>, Cu<sup>III</sup>CF<sub>3</sub> and Ag<sup>III</sup>CF<sub>3</sub> species,<sup>[2–4]</sup> along with their role in the trifluoromethylation of arylboron derivatives<sup>[3,4]</sup> and inactivated arenes<sup>[2c]</sup> through uncommon redox shuttles, will be presented.



**Figure 1.** Guiding principle of this seminar: Synthesis of high oxidation state MCF<sub>3</sub> complexes *via* 2e<sup>-</sup> oxidation step and its subsequent use for synthetic purposes (aromatic trifluoromethylation).

## References

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- [4] (a) Z. Lu, S. Liu, Y. Lan, X. Leng, Q. Shen, *Organometallics* **2021**, *40*, 1713. (b) L. Demonti, N. Saffon-Merceron, N. Mézailles, N. Nebra, *Chem. Eur. J.* **2021**, *27*, 15396.



## Dr. Noel NEBRA

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### EDUCATION

- 2009** **Ph.D in Organometallic Chemistry**, with honors, University of Oviedo, SPAIN.  
(*Cum Laude*)  
**Title:** "Development of New Catalytic Processes Promoted by  $\eta^3$ -Allyl Ru(II) and Ru(IV) Complexes: Selective Transformations of Propargylic Alcohols and N-Allyl amines."  
**Advisors:** Prof. José Gimeno and Dr. Victorio Cadierno.
- 2005** **Master Diploma in Science (Chemistry)**. University of Oviedo, SPAIN.
- 2004** **B.Sc. in Chemistry**. University of Oviedo, Spain.

### PROFESSIONAL RESEARCH EXPERIENCE

- 2014** **Tenured Scientist**, Chargé de Recherche Classe Normale du CNRS (LHFA, Toulouse, FRANCE). Team SHEN (headed by Dr. Nicolas Mézailles).
- 2013** **Post-doctoral associate** with Dr. Vladimir V. Grushin (ICIQ, Tarragona, SPAIN).  
Project entitled: "Fluorinated Organometallic Compounds in Synthesis and Catalysis."
- 2010** **Post-doctoral associate** with Dr. Didier Bourissou (LHFA, Toulouse, FRANCE).  
Project entitled: "New Pincer-Type Complexes Derived from 2-Indenylidene Ligands."

### FELLOWSHIPS, PUBLIC CONTESTS AND AWARDS

- 2021** **Young Investigator GEQO–RSEQ Award**.
- 2020** **Young Investigator ICT Award**.
- 2020** **JCJC-ANR grant** (Acronym: Ni4R<sub>F</sub>; PI: Dr. N. Nebra; Budget: ca. 280K €).
- 2014** **CNRS National Public Examination** (securing a CNRS tenured scientist position).
- 2013** **I.C.I.Q.-I.P.M.P. Marie-Curie Post-doctoral Grant** (2 years). Funding agency: CORDIS–European Commission and ICIQ.
- 2010** **I.E.F. Marie-Curie Post-doctoral Grant** (2 years). Project reference: FP7-PEOPLE-2009-IEF-253112-INDEN. Funding agency: CORDIS–European Commission.
- 2010** **F.P.U. Post-doctoral Grant** (2 years).
- 2010** **Ph.D Extraordinary Award**. Best Thesis in Chemistry conducted at University of Oviedo.
- 2006** **F.P.U. Pre-doctoral Grant** (4 years).

## BIBLIOMETRICS

[Citation Report based on SCOPUS Database (**December 3<sup>rd</sup>, 2021**)]

Number of Publications = **36**, including **1 Chem. Rev.**, **5 Angew. Chem.**, **2 J. Am. Chem. Soc.**, **2 ACS Catal.**, **4 Chem. Commun.**, **5 Chem. Eur. J.** & **1 Green Chem.**

Number of Book Chapters = **3**, *Wiley-VCH (2) & Nova Science Publishers (1)*.

Total Number of Publications included in First Quartile (Q1) = **29**.

Total Number of Citations = **1133**. Average per Item = **31.47**.

Average of Citations per Year = **66.65**.

Citations per Year received during the Last 10 Years = **98** (2012), **85** (2013), **73** (2014), **89** (2015), **76** (2016), **77** (2017), **82** (2018), **94** (2019), **96** (2020), **124** (2021). Average = **89.40**.

*h*-Index = **21**.

## CV SUMMARY

Dr. Nebra holds a CNRS Tenured Scientist position at LHFA (Toulouse, France), and works on the problem solving of industrially-relevant transformations (Cross-Coupling, Fluorine Chemistry, N<sub>2</sub>-functionalization,...) mediated by Organometallics. He was graduated in Chemistry at the University of Oviedo in June 2004, and prepared his Ph.D with Profs. J. Gimeno & V. Cadierno (**FPU Predoctoral Grant**). He investigated catalytic applications of allyl Ru complexes, with special focus on “*one-pot*” multistep organic transformations. He completed his Ph.D in June 2009, and received the **Best Thesis Award in Chemistry** (University of Oviedo).

Shortly after, Dr. Nebra was funded with a **FPU Postdoctoral Grant**, and later with the very prestigious, highly competitive **IEF Marie-Curie Postdoctoral Grant** to work with Profs. D. Bourissou & B. Martin-Vaca at Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA, Toulouse, France. Dec 2009–Feb 2013). Based on a ligand design strategy, he discovered unprecedented 2-indenediide Pd complexes and studied their unusual reactivity rules at the ligand backbone.

Afterwards, Dr. Nebra was appointed an **ICIQ-IPMP Marie-Curie Postdoctoral Researcher** working with Prof. V. Grushin at Institut Català d'Investigació Química (ICIQ, Tarragona, Spain. April 2013–Sept 2014). He thus achieved the synthesis, identification and characterization of Cu(III)CF<sub>3</sub> complexes, some of them being efficient in the oxidative trifluoromethylation of arylboronic acids.

Since 2015, Dr. Nebra develops his own research dealing with high-valent metal species [mainly Ni(III), Ni(IV) & Ag(III)] bearing *perfluorinated* ligands (F itself and CF<sub>3</sub>-groups). Preliminary results of this challenging chemistry were reported recently [ACIE **2017**, **56**, 12898 & *Chem. Eur. J.* **2021**, **27**, 15396 (**Hot Article & Inside Cover**)], representing the two first independent contributions of Dr. Nebra and the core of his research program, which was awarded by the French Agency of Research (ANR 2020 Call, acronym Ni4R<sub>i</sub>, *ca.* **€ 280K**, including Ph.D (1) + Postdoc (1) Grants).

Dr. Nebra has reported **32** research articles [**28** in Q1 (88%); including **2 JACS**, **5 ACIE** & **2 ACS Catal.**], **4** reviews (including **1 Chem. Rev.**) and book chapters (**3**). This work has received a number of citations (>**1100**) resulting in a steadily growing *h*-index of **21**. Dr. Nebra has performed reviewer tasks for the ANR (1), Scientific Journals (*ca.* **20**), and External Assessments for European Ph.D Distinctions (2). He has edited a Special Issue (Molecules), co-organized International Conferences (2) and given Oral Presentations at Conferences (8) and Universities (2). Recently, he has received the **2020 ICT Award** and the **2021 GEQO–RSEQ Award to Young Researchers**.