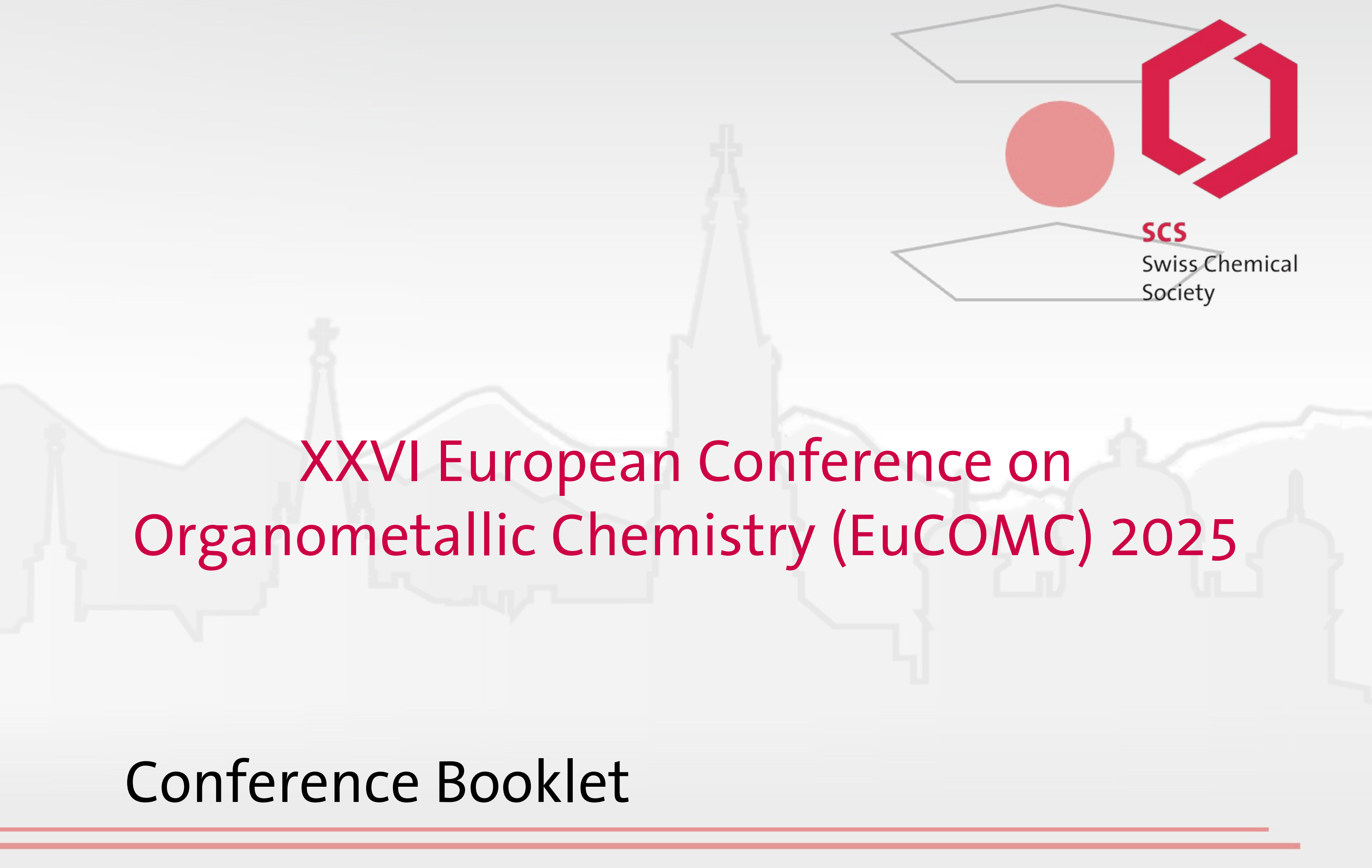


SCS
Swiss Chemical
Society

XXVI European Conference on Organometallic Chemistry (EuCOMC) 2025

Conference Booklet

Day 3: Tuesday July 8, 2025

General Sponsors and main supporters

NOVARTIS

syngenta

HELVETICA chimica acta

Chemistry A European Journal

EurJIC

Chemistry Europe

ACS Publications
Most Trusted. Most Cited. Most Read.

ORGANOMETALLICS

Organizers

EuChemS
European Chemical Society

UNIVERSITÄT BERN

Talks

Session 6

C-H Functionalization of Simple Arenes with Cooperating Pyridone Ligands: A Mechanistic View

A. C. Albéniz[1]

[1]IU CINQUIMA/Química Inorgánica. Universidad de Valladolid. 47071 Valladolid (Spain), Email: albeniz@uva.es

The direct use of arenes as coupling partners in palladium-catalyzed C–C bond-forming reactions is a sustainable alternative to the conventional cross-coupling processes.[1] These reactions eliminate the need to use either the main group organometallic reactant or the organic halide (sulfonate)—or even both reagents, saving the previous reaction steps required for their preparation. However, strong reaction conditions are generally required because a C–H activation step is needed, and it involves the coordination of the arene to the metal and the cleavage of the sluggish C–H bond. More active catalytic systems that functionalize simple arenes are needed to bring the undirected C–H functionalization closer to the mild conditions of the conventional cross couplings. To this end, the use of metal-ligand cooperation has proved to be a useful approach in C-H activation. We have been using chelating pyridone-type ligands such as 2,2'-bipyridin]-6(1H)-one (bipy-6-OH), and palladium complexes derived from this ligand enable C-H functionalization reactions of simple arenes (non-chelate assisted C-H activation) via the cooperating effect of the ligand in the C-H cleavage step.[2] Mechanistic studies have supported this fact and, once the C-H cleavage is facilitated, they have shown the importance of other steps in the catalytic cycle. Thus, bipy-6-OH also influences the product-forming step leading to interesting chemoselective coupling processes.[3] A mechanistically guided modification of the reaction conditions and catalyst composition leads to more active catalytic systems (use of suitable co-solvents or the use of a two-ligand system) or to unusual chemoslectivity. These approaches will be discussed, as well as their mechanistic implications, taking the direct arylation of simple arenes as model reaction.

Acknowledgments:
We acknowledge the financial support of the Spanish MICIU (AEI, grant PID2022-142100NB-I00), the joint support of the EU/MICINN/JCyL (C17.I01.P01.S21, H2MetAmo) and the Junta de Castilla y León (VA016G24).

[1] a) J. F. Hartwig, M. A. Larsen, *ACS Cent. Sci.* **2016**, 2, 281-292; b) T. Gensh, M. J. James, T. Dalton, F. Glorius, *Angew. Chem. Int. Ed.* **2018**, 57, 2296-2306; c) Y. Yang, J. Lan, J. You, *Chem. Rev.* **2017**, 117, 8787-8863; d) T. B. Gunnoe, W. L. Schinski, X. Jia, W. Zhu, *ACS Catal.* **2020**, 10, 14080–14092; e) W. Ali, G. Prakash, D. Maiti, *Chem. Sci.* **2021**, 12, 2735-2759.

[2] a) V. Salamanca, A. Toledo, A. C. Albéniz, J. Am. Chem. Soc. 2018, 140, 17851-17856; b) V. Salamanca, A. C. Albéniz, *Org. Chem. Fron*t. **2021**, 8, 1941-1951.

[3] C. Pinilla, V. Salamanca, A. Lledós, A. C. Albéniz, *ACS Catal.* **2022**, 12, 14527−14532.

Molecular Engineering of Earth-Abundant Metal Catalysts: An unexpected Journey into Metallaaromaticity

G. de Ruiter[1]

[1]Technion - Israel Institute of Technology

Ongoing efforts to advance sustainable chemistry have sparked renewed interest in using earth-abundant metals for homogeneous catalysis. Their natural abundance, low toxicity, and wide availability make them attractive alternatives to less sustainable noble metals. Furthermore, their smaller ionic radii and typically high-spin electronic structures enable distinct reactivity patterns that are often inaccessible with their heavier congeners. In this lecture, we will showcase how the unique properties of cobalt can be unlocked through rational ligand design. Specifically, we will highlight how subtle modifications in ligand architecture can shift the focus from developing efficient molecular catalysts to accessing unprecedented metallaaromatic species. Building on our previously reported $\mathrm{PC_{NHC}P}$ cobalt complexes, $[(\mathrm{PC_{NHC}P})\mathrm{CoMe}]$ (**1**) and $[(\mathrm{PC_{NHC}P})\mathrm{Co(N□)}]$ (**2**), we will first demonstrate their catalytic activity in the stereoselective isomerization of allyl ethers and allyl amines.[1] A key mechanistic feature of this transformation is a unique but reversible 1,2-alkyl migration from the cobalt center to the NHC ligand, which creates the necessary coordination space to facilitate catalysis.[2] We will then show how the reactivity of complex **2** can be redirected from alkene isomerization to [2+2] cycloaddition using α,ω-dienes, affording bicyclo-[3.2.0]heptanes via a cobalt-catalyzed pathway.[3] Finally, we will illustrate how transitioning from a $\mathrm{PC_{NHC}P}$ to an $\mathrm{NC_{NHC}N}$ ligand framework can significantly alter the physicochemical properties of the cobalt complexes. Particularly, we will show that, through ligand engineering, previously non-aromatic systems can be transformed into true metallaaromatic complexes via dative metal–ligand bonding. This aromatic character is supported by both experimental (notably downfield-shifted Co–Me ^{1}H NMR resonances) and computational analyses (NICS, ACID, and EDDB). Altogether, this work presents a new design paradigm, showing for the first time that metallaaromaticity can be accessed through coordination rather than classical covalent bonding, opening new avenues in organometallic chemistry.

References

[1] Sakthi Raje, Tofayel Sheikh Mohammad, Graham de Ruiter., *J. Org. Chem*. **2024**, *89*, 4319

[2] Sakthi Raje, Subhash Garhwal, Katarzyna Młodzikowska-Pieńko, Tofayel Sheikh Mohammad, Ron Raphaeli, Natalia Fridman, Linda JW Shimon, Renana Gershoni-Poranne, Graham de Ruiter., *JACS Au*, **2024**, *4*, 4234

[3]. Tofayel Sheikh Mohammad, Yi Jin, Sakthi Raje, Katarzyna Młodzikowska-Pieńko, Zhi-Xiang Yu, Graham de Ruiter., *J. Am. Chem. Soc*. **2025**, *147,* 15195

Talks

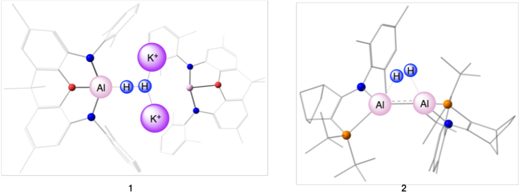
Session 7A

Mechanistic Insight into Oxidative Addition of H_2 to Al(I) Compounds

T. Krämer[1]

[1]School of Chemistry, Trinity College Dublin, College Green, Dublin 2, Ireland; e-mail: kraemert@tcd.ie

The activation of dihydrogen via H–H bond cleavage is not only a critical reaction relevant to an enormous range of catalytic processes, but also a fundamental transformation that is used as to benchmark the reactivity profiles of novel systems in small molecule activation.[1] As such, the elucidation of novel pathways for the activation of H2 is of widespread importance to scientists with interests as diverse as catalysis, organic/inorganic synthesis, and even energy storage. Within this sphere, the activation of E–H bonds (E = H, B, C, N etc.) by low-valent aluminium(I) carbene analogues has been the subject of significant research effort.[2] However, the reaction mechanisms of these reactions often remain contentious and poorly understood.



1

2

Figure 1. Activation of hydrogen by low-valent Al(I) complexes 1 and 2.

Combining computational quantum chemical and experimental studies, we have probed the mechanism for H_2 activation by two different Al(I) complexes, i.e. the K^+-stabilised contacted dimer pair $[K\{Al(NON)\}]_2$ (**1**, Figure 1)[3] and amidophophine-stabilised dialumene (**2**).[4] We propose two new mechanistic paradigms for these systems that directly contradict currently accepted classical models of single centre reactivity for carbene-like Al(I) species, i.e. those based on orbital interactions that mimic those of transition metals.[5] In the dimeric complex 1, H2 activation occurs via a frustrated Lewis pair (FLP)-type hydride rebound mechanism, with clear cooperativity between aluminium and potassium centres.[6] Activation of H_2 by **2** proceeds via stereoselective and concerted *anti*-addition to the Al=Al bond.[7] The new mechanistic proposals are extrapolated to related systems and are of wider significance for the catalytic application of Al(I) complexes in E-H bond activation.

[1] The Handbook of Homogeneous Hydrogenation (Eds.: J. G. de Vries, C. J. Elsevier), Wiley, Weinheim, **2006**.

[2] T. Chu, G. I. Nikonov, *Chem. Rev.*, **2018**, *118*, 3608.

[3] J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Nature* **2018**, *557*, 92.

[4] R. L. Falconer, K. M. Byrne, G. S. Nichol, T. Krämer, M. J. Cowley, *Angew. Chem. Int. Ed.*, **2021**, *60*, 24702.

[5] P. P. Power, *Nature* **2010**, *463*, 171.

[6] K. M. Byrne, J. Hicks, L. P. Griffin, S. Aldridge, T. Krämer, *Chem. Eur. J.*, **2025**, *31*, e202500095.

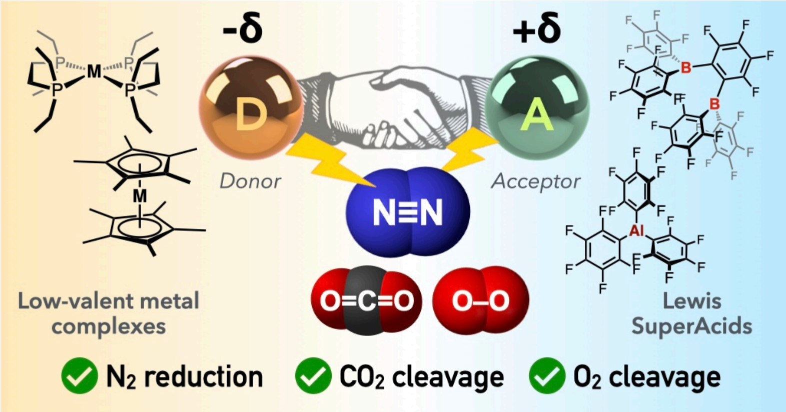
[7] Manuscript in preparation.

Implementing Lewis SuperAcids (LSA) in Hybrid Main Group/Metal Donor-Acceptor Systems for Small Molecules Activation

A. Simonneau[1], D. Specklin[1]*, M. Boegli[1]*, L. Escomel[1]*, M. Benonie[1]*, M. Grellier[1]*, M. Gennari[2]*, C. Duboc[2]*

[1]LCC-CNRS, Université de Toulouse, CNRS, UPS, 205 route de Narbonne, BP44099, F-31077 Toulouse cedex 4, France,
[2]Univ. Grenoble Alpes, CNRS UMR 5250, DCM, F-38000 Grenoble, France

Activation of small molecules by donor-acceptor systems is conceptually important as many catalytic processes rely on the synergistic action of electron-rich and -poor sites to activate and cleave bonds. This pertains to both the biological and industrial chemistry contexts. Inspired by the frustrated Lewis pair chemistry,[1] our team has developed dyads combining main-group Lewis acids with low-valent transition metal complexes, initially targeting N_2 activation.[2] Recently, we introduced Lewis superacids (LSA)[3] in those systems, such as $Al(C_6F_5)_3$ or Piers' bis(borane) *o*-$\{(C_6F_5)_2B\}_2C_6F_4$.[4,5] In this presentation, the influence of those extremely electron-deficient species in the activation of small molecules within hybrid molecular donor-acceptor systems will be discussed, benchmarking against the emblematic strong Lewis acid $B(C_6F_5)_3$. Notably, an emphasis on how LSA can be game-changers in small molecule activation by systems reminiscent of frustrated radical pairs will be made, to next embark on a discussion of the concept of Lewis acid coordination-coupled electron transfer (LACET).



[1] D. W. Stephan, Science, 2016, 354, aaf7229.

[2] A. Simonneau, R. Turrel, L. Vendier, M. Etienne, Angewandte Chemie International Edition, 2017, 56, 12268–12272.

[3] L. Greb, Chemistry – A European Journal, 2018, 24, 17881–17896.

[4] D. Specklin, M.-C. Boegli, A. Coffinet, L. Escomel, L. Vendier, M. Grellier, A. Simonneau, Chemical Science, 2023, 14, 14262–14270.

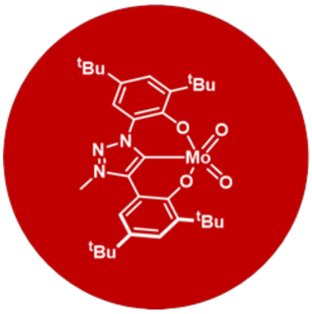
[5] L. Escomel, F. F. Martins, L. Vendier, A. Coffinet, N. Queyriaux, V. Krewald, A. Simonneau, Chemical Science, 2024, 15, 11321–11336.

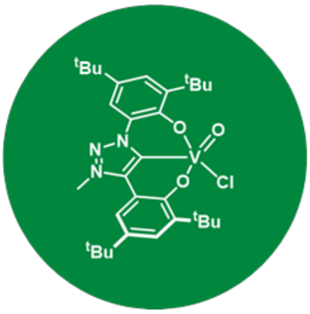
Utilizing Mesoionic Carbenes in Early Transition Metal Chemistry

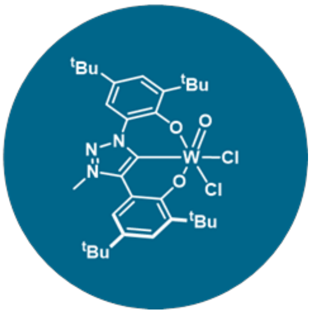
S. Hohloch[1]

[1]Department of General, Inorganic and Theoretical Chemistry, University of Innsbruck

Within the past decades, N-heterocyclic carbenes have taken a unique role in organometallic chemistry finding application in many fields of current synthetic chemistry and a plethora of subtypes emerged in the literature.[1] One of these subtypes are abnormal carbenes, nowadays better described as mesoionic carbenes.[2] First described by Crabtree *et al.* in the form of abnormally bound 4-imidazolylidenes,[3] the field exploded with the synthesis of 1,2,3-triazolylidene-based MICs by Albrecht *et al* in 2008.[4] The versatile synthesis of the 1,2,3-triazolylidene framework through the CuAAC reaction allowed for the preparation of a plethora of individual and tailored ligands for various applications in catalysis, photochemistry and coordination chemistry.[5]







However, when looking at NHCs/MICs ligands across the periodic table, the majority of their applications accumulates in the late transition metal regime, while early transition metal complexes have been barely investigated.[6] Here we present the versatility of anionic triazolylidene-based MICs in the chemistry of these barely investigated metals, showing their utility in catalysis and coordination chemistry with group V and group VI elements.[7]

[1] a) M.N. Hopkinson, C. Richter, M. Schedler, F. Glorius *Nature*, **2014**, *510*, 485. b) P. Bellotti, M. Koy, M.N. Hopkinson, F. Glorius *Nat. Chem. Rev.*, **2021**, *5*, 711.

[2] S.C. Sau, P.K. Hota, S.K. Mandal, M. Soleilhavoup, G. Bertrand *Chem. Soc. Rev.* **2020**, *49* 1233.

[3] S. Gründemann, A. Kovacevic, M. Albrecht, J.W. Faller Robert, H. Crabtree *Chem. Commun.* **2001**, 2274.

[4] a) P. Mathew, A. Neels, M. Albrecht *J. Am. Chem. Soc.*, **2008**, *130*, 13534. b) G. Guisado-Barrios, J. Bouffard, B. Donnadieu, G. Bertrand *Angew. Chem. Int. Ed.*, **2010**, *49*, 4759.

[5] a) R. Maity, B. Sarkar *JACS Au*, **2022**, 2, 22. b) W. Stroek, M. Albrecht *Chem. Soc. Rev.*, **2024**, *53*, 6322. c) G. Guisado-Barrios, M. Soleilhavoup, G. Bertrand *Acc. Chem. Res.*, **2018**, *51*, 3236.

[6] G. Horrer, M.J. Krahfuß, K. Lubitz, I. Krummenacher, H. Braunschweig, U. Radius *Eur. J. Inorg. Chem.*, **2020**, 281.

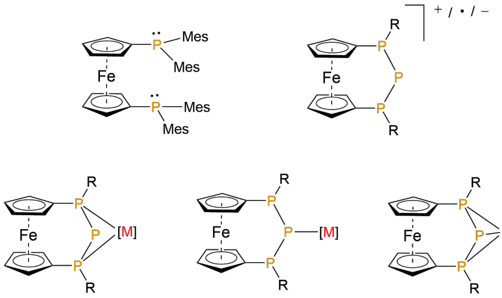
[7] a) M. Baltrun, F.A. Watt, R. Schoch, C. Wölper, A.G. Neuba, S. Hohloch *Dalton Trans.*, **2019**, *48*, 14611. b) F.R. Neururer, S. Liu, D. Leitner, M. Baltrun, K.R. Fisher, H. Kopacka, K. Wurst, L.J. Daumann, D.Munz, S. Hohloch *Inorg. Chem.*, **2021**, *60*, 15421. c) D. Leitner, F.R. Neururer, S. Hohloch *Dalton Trans.*, **2025**, *54*, 582. d) F.R. Neururer, F. Heim, M. Baltrun, P. Boos, J. Beerhues, M. Seidl, S. Hohloch *Inorg. Chem. Front.*, **2025**, DOI: 10.1039/D4QI02392G

Tuning the donor properties of ferrocene-based phosphorus ligands

R. Pietschnig[1]

[1]Institute for Chemistry, University of Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

In sterically encumbered dppf analogs the s-character of the lone-pair at phosphorus is reduced along with an increase of their donor ability.[1] The impact of this modification on the reactivity of thereof derived main group and transition metal complexes will be explored for bond activation processes and catalytic processes for hydroformylation or CO_2-derivatization.[2-6]



[1] S. Dey, R. Pietschnig, *Coord. Chem. Rev.* **2021,** *437*, 213850.

[2] R. Franz, D. Gál, C. Bruhn, Z. Kelemen, R. Pietschnig, *Adv. Sci.* **2024**, 2306805.

[3] S. Dey, B. Szathmári, R. Franz, C. Bruhn, Z. Kelemen, R. Pietschnig, *Chem. - Eur. J.* **2024**, e202400194

[4] S. Dey, D. Buzsáki, C. Bruhn, Z. Kelemen, R. Pietschnig, *Dalton Trans.* **2020,** *49*, 6668 – 6681.

[5] S. Dey, L. Dettling, D. Gál, C. Bruhn, Z. Kelemen, C. Müller, R. Pietschnig, *J. Catal.*, **2025**, *442*, 115871.

[6] D. Langgut, C. Bruhn, R. Pietschnig, *Chem. Eur. J.*, **2025**, accepted. https://doi.org/10.1002/chem.202500406

Ti(III) Organometallics with a Rigid Bis-Phenoxy NHC Pincer Ligand – Structures and Reactivity

I. Ligielli[1], G. Mitrikas[2]*, N. Tsoureas[1]*, R. A. Christopoulos[1]*, P. Kyritsis[1]*, A. A. Danopoulos[1]*

[1]Laboratory of Inorganic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens,
Panepistimiopolis Zografou GR-15771, Greece, [2]Institute of Nanoscience and Nanotechnology, N.C.S.R. "Demokritos",
15310 Athens, Greece

Compared to the ubiquitous organometallic chemistry of Ti(IV) supported by a wide range of spectator ligands, that of the lower oxidation states Ti(III) and Ti(II) is less explored, despite the expectation of diverse structures and reactivities to encompass open shell and/or highly reducing species.[1] Herein, we report on the synthesis, structures, and magnetic investigations of a new family of titanium complexes, bearing the rigid, non-innocent bis(phenoxide) pincer ligand with a C^{NHC} bridgehead (***L***).[2] Archetypal entries accessed were the octahedral [*trans*-Ti(***L***)Cl$(THF)_2$] and the tetrahedral [Ti(***L***)(amido)], amido = bis-(trimethylsilyl)-amido, aryl-trimethylsilyl-amido *etc*. Their substitution chemistry (salt metathesis or aminolysis, respectively) was frequently accompanied by redox changes at the Ti, reactivity at the Ti-C^{NHC} bond or bond scissions at the NHC heterocycle of the amido ligand. Reduction reactions of [*trans*-Ti(***L***)Cl$(THF)_2$] and [Ti(***L***)(amido)] by KC_8, also led to unexpected bond rearrangements. The mapping of the reactivities outlined was accomplished by the isolation and full characterisation (single crystal XRD, CW/pulse X-band EPR and NMR - where applicable - spectroscopies) of well-defined reaction product complexes. Computational studies have been used in a number of cases to give insight into the chemistry operating.[3],[4]

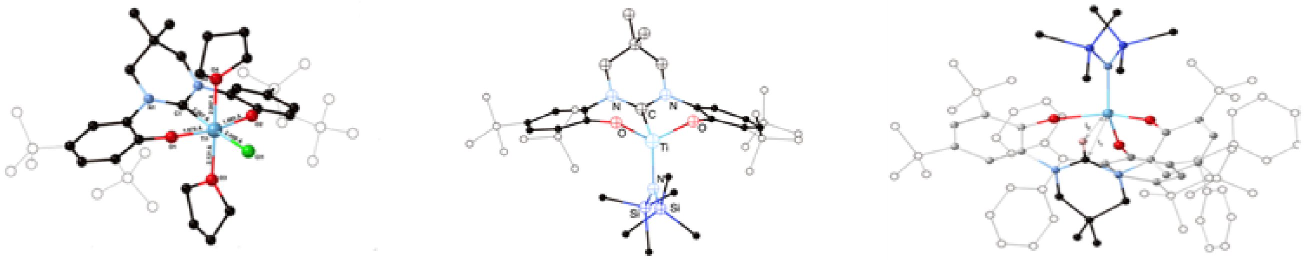


Figure 1: Molecular structures of [*trans*-Ti(***L***)Cl$(THF)_2$], [Ti(***L***)$\{N(SiMe_3)_2\}$] and product of aminolylis of the latter leading to Ti-C^{NHC} scission.

H.F.R.I.
Hellenic Foundation for
Research & Innovation

References

[1] X. Wu, Y. Chang, S. Lin, *Chem*, **2022**, 8, 1805-1821.

[2] F. He, K.P. Zois, D. Tzeli, A.A. Danopoulos, P. Braunstein, *Coord. Chem. Rev.*, **2024**, 514,215757.

[3] N. Rahimi, B. de Bruin, P.H.M. Budzelaar, *Organometallics*, **2017**, 36, 3189–3198.

[4] B. Stadler, Hilary H.Y. Meng, S. Belazregue, L. Webster, A. Collauto, K.M. Byrne, T. Krämer, F.M. Chadwick, *Organometallics*, **2023**, 42, 1278-1285.

Talks

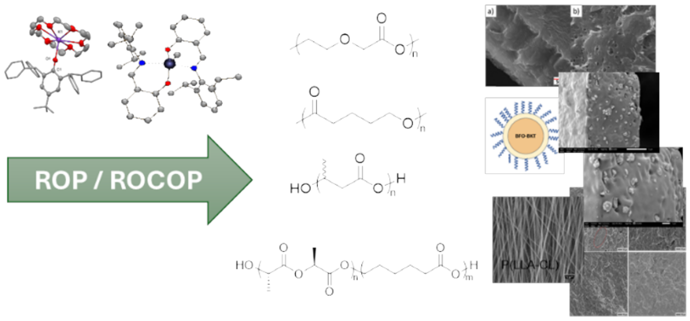
Session 7B

Synthesis of bio-based polymers with taylored properties using versatile main group catalysts

M. E. Mosquera[1], C. Rentero[1]*, D. Sánchez-Roa[1]*, V. Sessini[1]*, A. Medel[1]*, A. Leonés[1]*

[1]Universidad de Alcalá, Grupo SOSCATCOM, Departamento de Química Orgánica y Química Inorgánica, Facultad de Farmacia and Instituto de Investigación Química Andrés M. del Río (IQAR), Campus Universitario, Ctra. Madrid-Barcelona Km. 33,600, 28871 Alcalá de Henares, Madrid, Spain

Catalytic polymerization is a fascinating reaction influenced by many factors: the design of the catalyst, the monomers, the presence of co-initiators, the ratio amongst the reagents and the reaction conditions. In particular, Ring Openning Polymerization (ROP) is powerful reaction that offers a good control over the final microstructure of the polymers, hence it is a very good candidate to explore in detail the different aspects that controls the final microstructure and hence the properties of the polymers. Since the uses of the polymers would depend on their properties, different characteristics could be looked for, in terms of molecular weight or tacticity, so designing a versatile system that can allow the preparation of polymers with tailored properties is of high interest both for the academy and the industry. In our group we have longstanding experience in the preparation of main group metal complexes as catalysts for the ROP of cyclic esters to produce biobased polymers. Within main group metals, aluminum stands out as the most abundant metal on Earth crust and also has well known catalytic properties.[1] As well alkali metals such as Na and K are particularly attractive not only for their abundance but also due to their low toxicity. We have designed a series of aluminum and alkali metal complexes very active in catalytic ROP processes of rac-lactide, L-lactide and ε-caprolactone and alsoof a monomer quite reluctant to polymerize such as β -butyrolactone, both for homopolymerization and copolymerization. Besides they can attain polymer grafting to inorganic particles. Furthermore, by controlling the metal environment and the reaction conditions it is possible to synthesize polymers with controlled properties that can be used either as matrixes or as additives.[2]



Keywords
Ring-opening polymerization, Bio-based polymers, Catalysis, Earth abundant metals

[1] Fernandez-Millan, M. Temprado, J. Cano, T. Cuenca, M. E. G. Mosquera, Organometallics, 2020, 39, 2278-2286

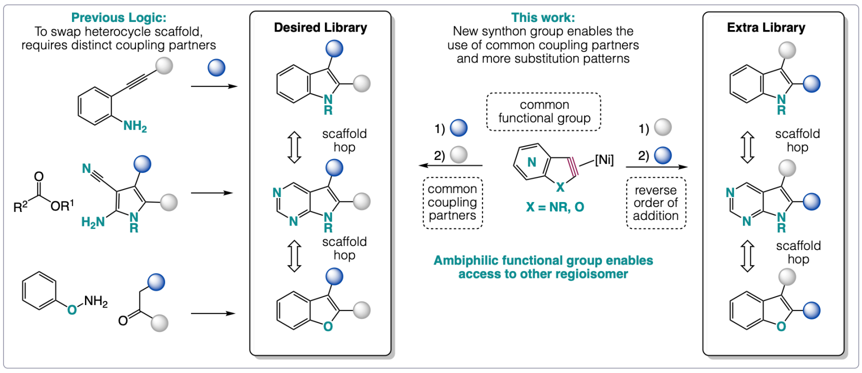
[2] E. G. Mosquera, J. Cano, S. Milione, S. et al., Organometallics, 2018, 37, 837. V. Sessini, M. Palenzuela, J. Damián, M. E. G. Mosquera, Polymer, 2020, 210, 123003; D. Sánchez-Roa, V. Sessini, M. E. G. Mosquera, J. Cámpora, ACS Catal. 2024, 14, 4, 2487–2501; M. Palenzuela, E. Mula, C. Blanco, V. Sessini, S. M. Guillaume, M. E. G. Mosquera, Macromol. Rapid Commun., 2024, 2400091; C. Rentero, H. Amorin, R. Jimenez, M. E. G. Mosquera, V. Sessini, *Polymer*, 2025,**325**, 128286.

Access to “Inaccessible” N-Heterocyclic Arynes Using Transition Metals

C. Roberts[1]

[1]University of Minnesota Department of Chemistry

Research in the Roberts group involves looking at unsolved problems in organic synthesis through the perspective of organometallic/inorganic chemistry. One main area of interest for the group is the synthesis of heterocycles through aryne intermediates. Despite their useful reactivity, a number of challenges still remain in the use of arynes including problems with regioselectivity and the synthesis of N-heterocyclic arynes. Using fundamental principles of Ni chemistry, our group is the first to be able to access previously “inaccessible” 5-membered heterocyclic arynes for the first time since they were hypothesized to exist 120 years ago. This talk will focus on those efforts.



[1] Humke, J. N.; Belli, R. G.; Plasek, E. E.; Kargbo, S. S.; Ansel, A. A.; Roberts, C.C., *Science*, **2024**, 408-414.

Understanding the Redox Chemistry of Aluminium

C. E. Weetman[1]

[1]University of Strathclyde, Glasgow, Scotland.

In the past ten years considerable progress has been made in low-oxidation state main group chemistry.[1] In particular, Low-oxidation state aluminium chemistry has flourished. From the isolation of neutral dialumenes and anionic aluminyls to exploiting Al(I) species in the activation of strong bonds via oxidative addition, such as those commonly found within waste emissions (e.g., C-O, C-F).[2] However, the high stability of the Al(III) oxidative addition product renders reductive elimination extremely challenging and currently prevents its use in redox catalytic processes.

Using a combined electrochemical and synthetic investigation, we have sought to understand the key electron transfer processes that are available to aluminium within different ligand systems. Initial studies have focused on β-diketiminate and *N*-heterocyclic carbene (NHC) stabilised aluminium complexes. Both reversible and irreversibler redox processes have been observed electrochemically,[3] whilst synthetically choice of reducing agent and NHC ligand are key. With Al(II) dialanes, Al(II) cations, asymmetric Al(II) dialanes and ligand exchange reactions all identified via NMR and single crystal X-ray diffraction studies.[4]

[1] C. Weetman and S. Inoue, *ChemCatChem*, 2018, 10, 4213-4228.

[2] K. Hobson, C. J. Carmalt, C. Bakewell, *Chem. Sci,* 2020, **11**, 6942-6956.

[3] F. Murphy, M. Bell, E. Aitken, B. McMillan, C. E. Weetman, *in preparation.*

[4] F. Murphy, A. R. Kennedy, C. E. Weetman, 2025, *Submitted.*

Luminescent organometallic materials using pyridylidene ligands for optoelectronic applications

J. Moussa[1]

[1]Sorbonne Université – Institut Parisien de Chimie Moléculaire UMR 8232 – Paris, France

Metal complexes of N-Heterocyclic carbenes (NHC) have found a plethora of applications in the last two decades following the seminal work of several groups. This contrasts with the underexplored pyridylidene category. Pyridylidenes exhibit a higher s-donor and p-acceptor character than imidazolylidenes, thus pyridylidenes are attractive ligands to promote organic transformations or light emission in the related transition metal complexes. Pyridylidenes remain scarcely investigated certainly due the absence of general methods for accessing pyridylidene-based metal complexes. Only few specific routes were reported to date. In this context our research investigations describe the development of several methods for the synthesis of organometallic compounds containing pyridylidene ligands with transition metals such as Ru(II), Os(II), Rh(III), Ir(III) and Pt(II). In particular, some of the complexes obtained exhibit strong phosphorescence in the solid state which makes them attractive candidates as doping materials in OLEDs to harvest the triplet excitons. Some of the non-metallated compounds exhibits TADF (Thermally Activated Delayed Fluorescence) which is of high interest in the third generation of OLED emitters. Moreover, our novel materials also show interesting NLO, catalytic and biological properties that are investigated in collaboration with several research groups. During this presentation, the development of our novel materials as well as the photophysical properties will be presented.

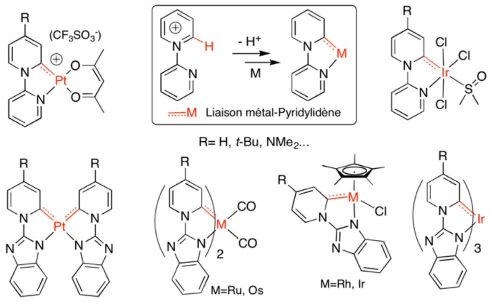


Figure: Archetypal structures of prepared compounds with pyridylidene ligands

1. Moussa, G. R. Freeman, J. A. Gareth Williams, L.-M. Chamoreau, P. Herson, H. Amouri, *Eur. J. Inorg. Chem.* **2016**, 76
2. Hassoun, A. Benchohra, O. Khaled, D. Seghouane, J. Moussa Monatshefte fuer Chemie **2020**, *151*, 799
3. Montagu, G. Gontard, J. A. G. Williams, J. Moussa *Eur. J. Inorg. Chem.* **2023** e202300487
4. Moussa, F. Julia, L.-M. Chamoreau, P. Gonzalez-Herrero *New. J. Chem.* **2024**, doi.org/10.1039/D3NJ05209E
5. S. Jamil, J. Moussa, *Coord. Chem. Rev.* **in press**

Molecular catalysts for alcohol homologation: the greener and the faster Guerbet reaction

R. Mazzoni[1,2], C. Lenzi[1,2]*, A. Piazzi[1,2]*, A. Messori[1,2]*, S. Pal[3]*, S. Kostera[3]*, L. Gonsalvi[3]*

[1]Dipartimento di Chimica Industriale “Toso Montanari”, University of Bologna, via Gobetti 85 40129 Bologna, Italy. , [2] Center for Chemical Catalysis – C3, University of Bologna, via Gobetti, 85 40129 Bologna, Italy., [3]ICCOM-CNR Via Madonna del Piano 10, 50019 Sesto Fiorentino (Fl) Italy

Bio-ethanol refining is conceived to develop new strategies to second-generation biofuels production. Among others, the Guerbet reaction is an attractive route for the catalytic upgrading of ethanol to linear and branched higher alcohols, which possess greater energy density and miscibility with conventional fuel compared to their lighter analogue. While simple in principle, this is difficult in application due to several concerns encountered in selectivity and conversion. These drawbacks can be partially avoided exploiting homogeneous catalysis.[1,2]

Within this field, our group recently developed a catalytic system based on a ruthenium based bifunctional molecular catalyst [Ru] containing cyclopentadienone as non-innocent ligand and an N-heterocyclic carbene to tune the redox properties, a base co-catalyst (NaOEt) and benzoquinone (BQ) as an additive able to promote unprecedented conversions toward the production of alcohol mixtures suitable for application as second generation bio-fuels or lubricants. The catalytic [Ru]/NaOEt/BQ triad well perform on bio-ethanol from waste (e.g. a real matrix from head and tail waste from alcohol distillation) and is water tolerant. Interestingly similar results can be achieved exploiting microwave heating. Scale up studies revealed an essential role of the reactor headspace. In order to extend the reactivity to pincer complexes never employed under these conditions, ruthenium and manganese P,N,N,N,P complexes have been tested, preliminary results show good conversions towards interesting reaction pathways.

Acknowledgements

We acknowledge financial support under the National Recovery and Resilience Plan (NRRP), Mission 4, Component 2, Investment 1.1, Call for tender No. 104 published on 2.2.2022 by the Italian Ministry of University and Research (MUR), funded by the European Union – NextGenerationEU– Project Title "Biomass-derived alcohols and polyols valorization and use by dehydrogenation/hydrogenation reactions promoted by bifunctional and proton-responsive homogeneous catalysts (ALCOVAL)". – CUP B53D23015120006 - Grant Assignment Decree No. n. 1064 adopted on 8/07/2023 by the Italian Ministry of Ministry of University and Research (MUR).

[1] Messori, A.; Gagliardi, A.; Cesari, C.; Calcagno, F.; Tabanelli, T.; Cavani, F.; Mazzoni, R. *Catal. Today* **2023**, *423*, 114003 and references cited therein.

[2] Cesari, C.; Gagliardi, A.; Messori, A.; Monti, N.; Zanotti, V.; Zacchini, S.; Rivalta, I.; Calcagno, F.; Lucarelli, C.; Tabanelli, T.; Cavani, F.; Mazzoni, R. *J. Catal.* **2022**, *405*, 47.

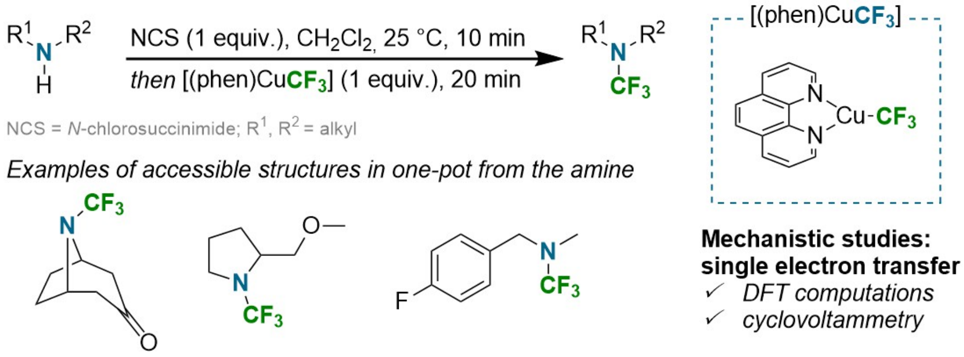
Copper-Mediated Trifluoromethylation of Amines

L. Anthore-Dalion[1], A. Touron[1]*, U. Todorovic[1]*, L. Severy[1]*, T. Cantat[1]*, E. Nicolas[1]*

[1]Université Paris-Saclay, CEA, CNRS, NIMBE, 91191 Gif-sur-Yvette, France

Introducing trifluoromethyl groups into bioactive molecules often has a dramatic effect on their properties, which is demonstrated by the increasing number of fluorinated-approved drugs.[1] Trifluoromethyl groups are mainly introduced as C–CF_3 linkages, but O–CF_3 and S–CF_3 linkages are also found. In contrast, *N*-trifluoromethyl amines are rarely studied, despite the ubiquity of nitrogen-containing compounds in the pharmaceutical industry. Historically, the lack of easy-to-implement synthetic pathways toward N–CF_3 bonds partly accounted for this absence, hampering more systematic studies of their reactivity, toxicity, and degradation pathways.[2]

In this work, we took advantage of a *Umpolung* strategy, by *in situ* converting the nucleophilic amine into its corresponding electrophilic chloramine, able to react with nucleophilic sources of CF_3. While the use of the Ruppert-Prakash reagent Me_3SiCF_3[3] led only to CF_3Cl, we have demonstrated that the well-defined copper(I) complex [(phen)$CuCF_3$] (phen=1,10-phenanthroline), developed by the group of Hartwig as trifluoromethylating reagent,[4] formed the targeted *N* -trifluoromethyl amines. Experimental mechanistic studies coupled with DFT computations have explained chloramines' ambident reactivity and the intriguing regioselectivity switch observed with [(phen)$CuCF_3$]. These insights unveiled that single electron transfers are the key players in activating the N–Cl bond.



[1] Jiang Wang, Maria Sánchez-Roselló, José Luis Aceña, Carlos del Pozo, Alexander E. Sorochinsky, Santos Fustero, Vadim A. Soloshonok, Hong Liu, *Chemical Reviews* **2014**, 114, 2432–2506.

[2] Stefan Schiesser, Hanna Chepliaka, Johanna Kollback, Thibaut Quennesson, Werngard Czechtizky, Rhona J. Cox, *Journal of Medicinal Chemistry* **2020**, 63, 13076–13089.[3] G. K. Surya Prakash, Andrei K. Yudin, *Chemical Reviews,* **1997**, 97, 757-786.[4] Hiroyuki Morimoto, Tetsu Tsubogo, Nichole D. Litvinas, John F. Hartwig, *Angewandte Chemie International Edition,* **2011**, 50, 3793–3798.