



Pincer Chemistry and Catalysis

Gerard van Koten,^{*,[a]} T. Keith Hollis,^{*,[b]} David Morales-Morales^{*,[c]}

This themed collection highlights the different and versatile applications of pincer metal compounds in modern chemistry, ranging from chemical biology to catalysis, including the activation of small molecules, diverse organic synthesis applications

and electrochemistry. These works serve as an illustration of the richness and state of the art of current research in pincer metal chemistry and catalysis, amply demonstrating the abundant opportunities and future prospects of the field.

The discovery of pincer^[1] metal compounds by Moulton & Shaw in 1976,^[2] introduced, in the scenario of organometallic chemistry, a new privileged ligand scaffold^[3] for the production of a plethora of new metal complexes that over time have found a large number of applications,^[4] this being particularly true in the case of homogeneous metal-catalyzed processes.^[5] This amazing development has been promoted by their inherent physical and chemical properties that allow these pincer-metal complexes to withstand higher temperatures which enable them to activate very strong chemical bonds that would otherwise be difficult to convert. In recent years this fact has become particularly relevant for the activation and conversion of relatively inert molecules such as carbon dioxide and methane into high value products, serving in this way at the same time as a promising palliative for very important issues such as global warming.^[6]

Evolution of this chemistry has led to multiple, creative modifications of the original pincer ligand backbone, extending the original definition to include, not just the classical organometallic PCP ligands (denomination given by the way the pincer's three donor sites typically coordinate to its metal site),^[7] but many other donor atoms in the side arms (N, S, O, etcetera). More importantly, the variation of the central atom by, for instance, nitrogen or silicon, has resulted in the discovery of the so-called non-innocent behavior of the resulting pincer ligands, involving

active metal-ligand cooperation between the pincer ligand and the connected metal site.^[8] The participation of active pincer-metal cooperation in pincer-metal catalysts opened up novel avenues for the intimate reaction steps during a catalytic cycle. These new observations have also facilitated the use of other, more abundant, cheap, first row transition metals such as manganese, cobalt, and iron, thus allowing the further "greening" of catalytic processes involving pincer-metal catalysts. This evolution has not stopped here.^[9] In recent years a surprising and exciting discovery was the participation of pincer-metal complexes in biological systems.^[10] The versatility and facile modification of the pincer backbone has also allowed the use of this ligand platform in many other applications beyond catalysis, such as for the development of sensors and to mimic some biological transformations.^[11]

It is because of these ongoing developments that Chemistry Europe promoted the publication of this Special Collection by the joint effort of two of their most iconic journals, the *European Journal of Inorganic Chemistry* and *ChemCatChem*, launching a call for papers to specialists around the world to contribute with their latest exciting chemistry. This themed collection highlights the different and versatile applications of pincer metal compounds in modern chemistry, ranging from catalysis to chemical biology. Internationally recognized authors from different laboratories throughout Europe, Asia and the Americas have contributed to produce an exciting collection of excellent papers. All aspects of pincer catalysis are represented herein; from the activation of small molecules through a range of organic synthesis applications and on to electrochemistry. These works serve as an illustration of the richness and state of the art of current research in pincer metal chemistry, with multiple applications and covering most areas of chemistry; each contribution underlining the prospect that still many other applications are to be discovered.

This Special Collection would not have been a success without the enthusiastic and invaluable contributions of the many authors and reviewers, as well as of the highly professional Editorial Teams of the *European Journal of Inorganic Chemistry* and *ChemCatChem*. We sincerely hope that their readers find this collection interesting and an inspiration for further developments in pincer metal chemistry which is a research field full of opportunities.

[a] *Organic Chemistry and Catalysis, Debye Institute for Materials Science
Faculty of Science, Utrecht University
3584CG Utrecht, The Netherlands
E-mail: g.vankoten@uu.nl
https://www.uu.nl/en/research/prof-dr-gerard-van-koten*

[b] *Department of Chemistry
Mississippi State University
MS 39762 Mississippi State, United States
E-mail: khollis@chemistry.msstate.edu*

[c] *Instituto de Química
Universidad Nacional Autónoma de México
Circuito Exterior, Ciudad Universitaria
04510 Ciudad de México, Mexico
E-mail: damor@unam.mx
https://iquimica.unam.mx/david-morales-morales*

ORCID(s) from the author(s) for this article is/are available on the WWW under <https://doi.org/10.1002/ejic.202000858>.

This manuscript is part of the Special Collection Pincer Chemistry and Catalysis.

Gerard van Koten is Honorary Distinguished University Professor of Utrecht University. He is member of the Royal Netherlands Academy of Arts and Sciences (KNAW). He is well known for his ground breaking fundamental and applied research on Pincer metal complexes, a field of research that his research group started during the early 1970s. Preparation and use of the first examples of homogeneous metallo-dendrimer catalysts demonstrate his interest for supramolecular systems with organometallic, catalytically active, functionalities. More recent developments involved the introduction of Pincer metal units, either functioning as sensor or as catalyst, in polypeptide chains, in carbohydrates and in the active site of serine hydrolases.



T. Keith Hollis is Professor of Chemistry at Mississippi State University. He completed his Ph.D. under the guidance of the late Professor Brice Bosnich at The University of Chicago in 1995 developing transition metal Lewis acid catalysts and studying their mechanisms. Subsequently, he completed an NIH postdoctoral fellowship with Professor Larry E. Overman at the University of California, Irvine, developing some of the first examples of the enantioselective allylic imidate rearrangement catalysts. He began his independent career developing novel organometallic complexes and studying their applications to a wide array of reactions as catalysts and for materials applications. In 2004 his research team developed the first examples of



CCC-NHC bis-carbene pincer complexes and began studying their chemistry. They continue expanding the realm of known metal examples of this ligand architecture and its applications today with a particular focus on sustainable energy issues.

David Morales-Morales earned his BSc and MSc degrees from the Chemistry School of the Universidad Nacional Autónoma de México (UNAM) and his PhD degree from the University of Essex (1998) under the supervision of Prof. Dr. Jonathan R. Dilworth on organometallic chemistry and catalysis. After a postdoctoral stay in Prof. Dr. Craig M. Jensen's group at the University of Hawaii at Manoa, he took his current position at the Instituto de Química-UNAM. His research interests lie in the realm of coordination and organometallic chemistry and their applications, with special emphasis on the chemistry of pincer compounds, the synthesis of phosphorus- and sulfur-based compounds and their use as ligands with transition metals, metal-mediated organic synthesis, mechanistic studies, catalysis, and medicinal chemistry. He has been part of the advisory board of the International Symposium on Homogeneous Catalysis (ISHC) and of the journals *ChemCatChem* (Wiley), *SN Applied Sciences* (Springer), *Current Organic Chemistry* and *Clinical Cancer Drugs* (Bentham) and has served as the editor of the books *The Chemistry of Pincer Compounds* (co-edited with C. M. Jensen, Elsevier, 2007) and *Pincer Compounds. Chemistry and Applications* (Elsevier, 2018) and currently for the journal *Current Organic Synthesis* (Bentham).



Acknowledgements

The financial support for D.M–M research by PAPIIT-DGAPA-UNAM (PAPIIT IN210520) and CONACYT A1-S-33933 is gratefully acknowledged.

- [1] G. van Koten, *Pure Appl. Chem.* **1989**, *61*, 1681–1694.
- [2] C. J. Moulton, B. L. Shaw, *J. Chem. Soc. Dalton Trans.* **1976**, 1020–1024.
- [3] G. van Koten, R. A. Gossage (Eds.), *The Privileged Pincer-Metal Platform: Coordination Chemistry & Applications in Top. Organomet. Chem.* Vol. 54, Springer, Heidelberg, **2016**.
- [4] D. Morales-Morales, C. M. Jensen (Eds.), *The Chemistry of Pincer Compounds*, Elsevier, **2007**.
- [5] a) D. Morales-Morales, H. Valdes, M. A. García-Eleno, D. Canseco-Gonzalez, *ChemCatChem* **2018**, *10*, 3136–3172; b) M. Asay, D. Morales-Morales, *Dalton Trans.* **2015**, *44*, 17432–17447; c) H. Valdes, E. Rufino-Felipe, D. Morales-Morales, *J. Organomet. Chem.* **2019**, *898*, 120864; d) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759–1792.
- [6] a) J. D. Cope, N. P. Liyanage, P. J. Kelley, J. A. Denny, E. J. Valente, C. E. Webster, J. H. Delcamp, T. K. Hollis, *Chem. Commun.* **2017**, *53*, 9442–9445; b) X. Zhang, A. M. Wright, N. J. DeYonker, T. K. Hollis, N. I. Hammer, C. E. Webster, E. J. Valente, *Organometallics* **2012**, *31*, 1664–1672.
- [7] G. van Koten, D. Milstein (Eds.), *Organometallic Pincer Chemistry in Top. Organomet. Chem.*, Vol. 40, Springer, Heidelberg, **2013**.
- [8] Recent paper and review: a) D. Oren, Y. Diskin-Posner, L. Avram, M. Feller, D. Milstein, *Organometallics* **2018**, *37*, 2217–2221; b) J. R. Khusnutdinova, D. Milstein, *Angew. Chem. Int. Ed.* **2015**, *54*, 12236–12273.
- [9] D. Morales-Morales (Ed.), *Pincer Compounds Chemistry and Applications*, Elsevier, **2018**.
- [10] B. Desguin, T. Zhang, P. Soumillion, P. Hols, J. Hu, R. P. Hausinger, *Science* **2015**, *349*, 66–69.
- [11] a) M. Albrecht, G. van Koten, *Angew. Chem. Int. Ed.* **2001**, *40*, 3750–3781; b) M. K. Salomón-Flores, I. J. Bazany-Rodríguez, D. Martínez-Otero, M. A. García-Eleno, J. J. Guerra-García, D. Morales-Morales, A. Dorazco-González, *Dalton Trans.* **2017**, *46*, 4950–4959.

Received: September 10, 2020