

Exotic metal complexes and their reactivity – chemistry when anions are (almost) absent

Cationic metal complexes constitute a very large and important group of chemical entities that have aroused interest due to their structure often containing atypical bonds but also due to their key role in numerous reactions and practical applications. For this reason, their synthesis, modification of properties and understanding of reactivity is an important element of research at both the fundamental and application levels. One of breakthroughs in the development of metal cation chemistry was the introduction of the so-called weakly coordinating anions, which, thanks to their structure, allowed for the synthesis of cationic species characterized with high reactivity or very low stability. [1]

In this presentation I will discuss a number of new metal complexes that have been obtained using perfluorinated alkoxalates, $\{\text{Al}[\text{OC}(\text{CF}_3)_3]_4\}^-$, as very weakly basic (in the Lewis' sense) counterions. The scope of the discussed systems will include monovalent or divalent metal cations ligated with molecules of low Lewis basicity, such as nitromethane, halogenated acetonitriles,[2] dinitrogen molecule,[3] or a noble gas atom. Some of these compounds exhibit interesting catalytic properties in the important and often demanding organic reactions like Diels-Alder cycloadditions, or hydrosilylations.[4] It turns out that in some cases the mechanism of the reaction is different from those reported so far, which shows the potential of salts of weakly coordinating anions in the development of modern chemistry.

[1] I. M. Riddlestone, A. Kraft, J. Schaefer, I. Krossing, *Angew. Chem. Int. Ed.*, 2018, 57, 13982.

[2] M. J. Jadwiszczak, P. J. Malinowski, *Chem. Eur. J.*, 2023, 29, e202202976

[3] J. Willrett, M. Schmitt, V. Zhuravlev, M. Sellin, P. J. Malinowski, I. Krossing, *Angew. Chem. Int. Ed.*, 2024, 63, e202405330.

[4] M. Grochowska-Tataczak, K. Koteras, K. Kazimierczuk, P. J. Malinowski, *Chem. Eur. J.*, 2024, 30, e202401322.