

## Organometallic Chemistry within Metal–Organic Frameworks

The chemistry of metal–organic frameworks (MOFs) has seen exponential growth over the past 20 years. While early efforts in this field sought to expand the structural diversity of these molecule-inspired solids, a series of recent developments now indicate that MOFs also offer a fertile space for innovation in organometallic chemistry. In recognition of these new developments, we present this *Organometallics* Special Issue, “Organometallic Chemistry within Metal–Organic Frameworks”. We hope this collection of articles will help better inform the research community about this research trend and, at the same time, remind our readership that *Organometallics* welcomes these types of manuscripts, as we seek to be the leading publication for new directions surrounding the chemistry of the metal–carbon bond.

Organometallic chemistry has emerged in the backbone of the coordination networks that make up MOF structures. Most MOFs are coordination solids obtained upon the combination of metal ions with an organic linker bearing nitrogen or oxygen donor atoms. However, the advent of new polyfunctional carbon-based linkers, for example with isocyanides as donor functionalities, show that the organometallic M–C bond can also be used to connect these extended structures.<sup>1</sup> Organo–main-group compounds have also made their entry into MOFs. A common strategy involves the synthesis of a linker bearing a main-group unit, which after combination with metal ions becomes part of the MOF architecture. The organo–main-group unit, containing elements such as boron or phosphorus, may play a geometrical role and influence the structure of the MOF. These units may also provide sites for subsequent chemistry, especially when the main-group element is a Lewis basic pnictogen that can be oxidized or coordinated to metals.

Humphrey and co-workers have been especially active in this area, as illustrated by their contribution in which they describe a new entry into the synthesis of coordination materials with low-valent metals bound to phosphines (DOI: 10.1021/acs.organomet.9b00319). Their contribution is innovative in that the low-valent metal is pre-coordinated to the phosphine prior to addition of the cross-linking, hard metal ions that cement the network. This appealing synthetic strategy will likely provide access to a broad range of materials with unprecedented structures and reactivities.

Building on this strategy, specific efforts have been dedicated to the installation of ligands within the linkers. These ligands may include classical chelating motifs, which can then be metalated post-synthetically. Using this strategy, a collaborative team involving Champness, Sumby, and Doonan describes the installation of  $[\text{Mn}(\text{CO})_3\text{Br}]$  at an N–N' chelation site presented by methylene-bridged bis(pyrazolyl) ligands (DOI: 10.1021/acs.organomet.9b00401). This approach allows the researchers to position  $\text{L}_2\text{MnCO}_3\text{Br}$  complexes within the solvent-accessible interior of a MOF. Taking advantage of single-crystal to single-crystal transformations, the team shows that polar solvents stabilize the cationic manganese center, leading to structures of the general formula  $[\text{L}_2\text{MnCO}_3\text{L}']^+$ , while less polar solvents favor the formation of the bromide-

bound form of the complex. The speciation of the manganese complexes within the MOF does not follow that of homogeneous analogues, thereby reflecting the unique environment provided by the MOF interior with respect to adjusting the coordination sphere of the metal atom.

The covalent attachment of widely used PCP or PNP pincer ligands within a MOF structure has also been realized, as for example by the Wade group, who describes MOF-containing accessible PNP–Ru complexes (DOI: 10.1021/acs.organomet.9b00482). In much the same way as for their homogeneous counterparts, the ruthenium center of these immobilized complexes can be converted via ligand abstraction reactions into a catalyst that promotes the hydrosilylation of aldehydes. Along similar lines, the Martin-Matute group offers a streamlined approach to PCN-222 using microwave techniques and establishes the advantage of this method by accessing a family of MOFs that differ in the nature of the first-row transition metal immobilized in the porphyrin core (DOI: 10.1021/acs.organomet.9b00273). This contribution culminates with a demonstration that the resulting materials catalyze the cycloaddition of epoxides and azidines with  $\text{CO}_2$ .

In an interesting variant of these approaches, a team led by Powers shows that appropriately functionalized diruthenium paddlewheel complexes can be copolymerized with polyalkynes via classical Sonogashira strategies (DOI: 10.1021/acs.organomet.9b00162). The result is a family of porous materials featuring a diruthenium unit incorporated within a highly cross-linked covalent framework. Although the materials are amorphous, they display significant porosity and can be used to catalyze intramolecular alkene hydroamination reactions, the chemoselectivity of which can be controlled by the ligand used in the paddlewheel dinuclear core. These results, and in particular the Sonogashira coupling strategy, set the stage for future efforts in which catalytically active homogeneous complexes are converted into immobilized and recyclable materials.

Organometallic chemistry can also take place at the metal ions present in the secondary building units (SBUs) of MOFs, as demonstrated by Volkmer and co-workers, who report the installation of anionic hydrocarbon ligands directly at the node of the pentanuclear Kuratowski-type SBU of MFU-4-type MOFs (DOI: 10.1021/acs.organomet.9b00297). While all structures possessing Zn–C bonds display remarkable chemical stability, including under ambient conditions, the structures with Co– $\text{CH}_3$  motifs are prone to hydrolysis, providing an elegant entry into the corresponding Co–OH species. This organometallic precursor approach to cobalt hydroxide affords a system with a  $\text{CO}_2$  absorption capacity comparable to that of carbonic anhydrase. Such materials are attracting increasing interest as  $\text{CO}_2$  sequestering agents.

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Upon activation, metal ions of the SBUs in some MOFs can become coordinatively unsaturated and thus are prone to reaction or interaction with incoming molecules. For example, the coordination of CO can alter the electronics of the metal center.<sup>2</sup> These exposed metal ions may also provide a site for the coordination of hydrocarbon molecules of various degrees of unsaturation. Alkenes and alkynes are well-known ligands in molecular organometallic chemistry and have logically also been observed as entities coordinated to exposed metal sites within MOFs.<sup>3</sup>

What may be more surprising is the coordination of alkanes accessed either by the interaction of hydrocarbons with the MOF or by solid-state hydrogenation reactions starting from the corresponding alkene complexes.<sup>4</sup> The isolation of alkane complexes is a noteworthy achievement, because such species are usually remarkably elusive and have only rarely been characterized in the condensed state when molecular complexes are employed.<sup>5</sup> The lack of competing solvents for the metal sites as well as the rigidity of the environment provided by the three-dimensional structure are essential features that make MOFs well-suited for the isolation and study of organometallic complexes otherwise too labile to isolate. Because the affinity of the metal site for a given hydrocarbon can be adjusted, the organometallic interaction occurring in these MOFs can be used as a basis for new hydrocarbon separation technologies.<sup>4</sup>

The contribution of Johnson's group to this Special Issue illustrates some of these concepts (DOI: 10.1021/acs.organomet.9b00351). Combining experiment and theory, this group reports how Cu(I)-MFU-4l, a MOF with isolated three-coordinate Cu(I) centers, shows a high affinity for small organometallic ligands such as CO, ethylene, and propylene. The study reveals that only one ligand molecule binds to each site, thereby mimicking the characteristics of classical organometallic complexes.

These results highlight the potential of organometallic interactions for application in gas separations and possibly catalysis. Indeed, the exposed metals present at the SBUs can also be sufficiently reactive to not only bind but also activate hydrocarbons, thus opening the door to classical organometallic reactions, including olefin oligomerization and polymerization reactions.<sup>6</sup> The chemistry that occurs here is unique in that it takes place in the gas phase, with the open metal site acting as a heterogeneous catalyst. However, unlike organometallic catalysts immobilized on surfaces, the organometallic reaction occurs within the MOF interior, thereby offering the possibility for increased selectivity based on steric effects associated with the pore geometry.

MOFs can also serve as matrices for the covalent or noncovalent immobilization of organometallic complexes and catalysts, the properties of which can benefit from the new environment offered by the MOF. The back-to-back contributions of Chmielewski and Grela on the immobilization of a commercially available ruthenium olefin metathesis catalyst provide a clear illustration of this possibility.

Chmielewski and co-workers show that the catalyst can be immobilized using simple acid–base chemistry between (Cr)MIL-101-SO<sub>3</sub>H, a MOF with internal sulfonic acid functionalities, and the metathesis catalyst, which possesses a peripheral amino group (DOI: 10.1021/acs.organomet.9b00281). This elegant approach results in a robust system where the immobilized catalyst retains its high activity and can be easily separated from the reaction products by

simple filtration. Grela and co-workers report the immobilization of the same catalyst, albeit via a slightly different approach (DOI: 10.1021/acs.organomet.9b00287). Rather than relying on simple Brønsted acid–base chemistry, immobilization is achieved via ion exchange, using (Cr)MIL-101-SO<sub>3</sub>-Na<sup>+</sup> and a methylated and thus a cationic version of the catalyst. This ion exchange reaction affords an immobilized metathesis catalyst that retains high activity and selectivity in reactions involving functionalized substrates.

Using a strategy that also rests on the use of electrostatics, a team led by Ma describes the immobilization of a cationic trinuclear palladium complex within the pores of Bio-MOF 100, an anionic metal–organic framework (DOI: 10.1021/acs.organomet.9b00286). The resulting materials catalyze the semihydrogenation of alkynes and show good recyclability. The same reaction is also promoted by the Rh-Ga/NU-1000 material recently described by Lu and colleagues. In this Special Issue, Lu's group in collaboration with Farha and co-workers takes a detailed look at this MOF-based alkyne semihydrogenation catalyst and shows that mechanistic probes usually employed for homogeneous systems can also be used to shed light on the nature of the reaction occurring at the immobilized catalyst (DOI: 10.1021/acs.organomet.9b00331).

In another unique development, at the confluence of organocatalysis and MOF chemistry, Cui, Liu, and co-workers describe an approach to asymmetric catalysis that relies on the copolymerization of methyl acrylate and proline acrylate inside MIL-101(Cr) (DOI: 10.1021/acs.organomet.9b00277). A remarkable property of the resulting composites, rendered internally chiral by the presence of the proline-containing polymer, is their ability to catalyze asymmetric aldol reactions with high enantioselectivities and diastereoselectivities.

We hope that this Special Issue will help fortify the connections that exist between classical organometallic chemistry and MOF chemistry and lead to new avenues for exploring this unique chemistry. We are grateful to all the contributors and encourage the MOF community to consider *Organometallics* as a primary venue for the publication of their research.

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### Notes

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## ■ EDITOR'S NOTE

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