

## Preview

# Frustrated Lewis Pair Chemistry Meets Metal-Organic Frameworks

Douglas W. Stephan<sup>1,\*</sup>

In this issue of *Chem*, Ma and coworkers meld metal-organic framework (MOF) chemistry with the emerging field of main-group catalysis for the first time. A MOF-supported Lewis pair is prepared, characterized, and shown to be an effective, stable, recyclable, and selective catalyst for hydrogenation.

Metal-organic frameworks (MOFs) are an area of chemistry that has risen to prominence over the past 20 years.<sup>1</sup> This family of materials comprises three-dimensional solids derived from metal ions and linking organic ligands. Such solids are robust, porous, and highly tunable. Initial applications exploited the capacity of MOFs to store gases at relatively high densities as a result of their porosity. This led to numerous studies involving the uptake and storage of gases<sup>2</sup> such as H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, PH<sub>3</sub>, and BH<sub>3</sub>. The ready synthesis of a large variety of MOFs has allowed functionalization for a broadened range of applications, including sensing, gas separation, and catalysis.<sup>3</sup>

In the last area, a vast array of homogeneous catalysts have been developed in the 20<sup>th</sup> century and have provided exquisitely selective processes for the synthesis of numerous fine chemicals, from pharmaceuticals and polymers to agro-chemicals and advanced materials. However, adaptation of such molecular catalysts for commercial processes often demands grafting these catalysts to heterogeneous supports in order to enhance catalyst stability and expedite both product-catalyst separation and catalyst recycling. The advent of MOFs has provided a new support material, one that is ideally suited to heterogeneous catalysis. In contrast to

most other supports, MOF supports provide a large internal surface area that is systematically tunable. Variations in the pore size or the metals incorporated in the MOF provide avenues for tuning both the catalyst reactivity and the selectivity.

Into the 21<sup>st</sup> century, the development of both homogeneous and heterogeneous catalyst design was principally limited to systems based on transition-metal chemistry. However, in 2006, this paradigm was broadened when combinations of main-group Lewis acids and bases in which conventional dative bonding was sterically inhibited were shown to effect hydrogen activation.<sup>4</sup> This finding led to the application of so-called “frustrated Lewis pairs” (FLPs) in catalytic hydrogenations, reactions previously perceived as exclusive to the realm of transition-metal catalysis.<sup>5</sup> Since these seminal papers, a large number of studies have probed the reactions of FLPs with a wide variety of small molecules, including olefins, alkynes, CO<sub>2</sub>, CO, NO, SO<sub>2</sub>, and N<sub>2</sub>O, among others.<sup>6,7</sup> At the same time, the range of FLPs that effect catalytic hydrogenation has broadened dramatically. This has allowed for the metal-free reduction of an increasing range of organic substrates, increased the tolerance for functional groups, and extended FLPs systems to effect enantioselective reductions. Such advances have

garnered attention in part because of the novelty of metal-free hydrogenation catalysis. This work has also been driven by the prospect of products free of metal contaminants, addressing concerns over the paucity and cost of precious-metal catalysts, the toxicity of residual metals, and the cost associated with product purifications. That being said, implementation of such metal-free catalysts faces the same concerns as for other homogeneous catalysts: stability, recyclability, and catalyst-product separation. It is for this reason that the notion of exploiting MOFs to support FLP catalysts is an attractive one.

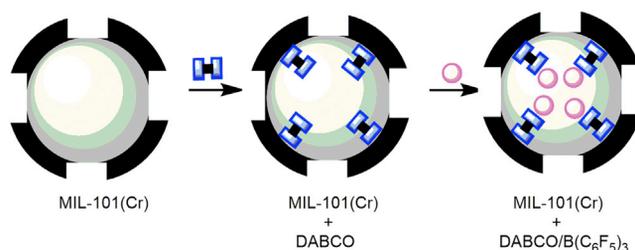
In this issue of *Chem*, Ma and coworkers<sup>8</sup> describe a remarkably clever and facile strategy that incorporates Lewis pairs (LPs) into a MOF framework. The dehydrated MOF, MIL-101(Cr),<sup>9</sup> Cr<sub>3</sub>(OH)O(BDC)<sub>3</sub> (BDC = 1,4-benzenedicarboxylate), selected for its stability and large pore size, was exposed to a solution of 1,4-diazabicyclo[2.2.2]octane (DABCO), resulting in the binding of the base to the open metal sites in the pores of the MOF. This left the remaining nitrogen atoms of the DABCO ligand exposed in the pores. Subsequent exposure to B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> resulted in the incorporation of the Lewis acid, affording encapsulation of the LP (DABCO)/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> into the MOF (Figure 1).

This new material, designated MIL-101(Cr)-LP, was characterized by a series of techniques. Powder X-ray diffraction (PXRD) measurements and N<sub>2</sub> gas sorption at 77 K affirmed the preservation of the framework structure and confirmed the anticipated decrease in pore size due to the presence of the LPs. Spectra obtained by Fourier

<sup>1</sup>Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, ON M5S 3H6, Canada

\*Correspondence: [dstephan@chem.utoronto.ca](mailto:dstephan@chem.utoronto.ca)  
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**Figure 1. Schematic Showing the Synthesis of MIL-101(Cr)-LP**

transform infrared spectroscopy and X-ray photoelectron spectroscopy were consistent with the presence of DABCO and the perturbation of the metal sites of MIL-101(Cr). Scanning electron microscopy and transmission electron microscopy showed that MIL-101(Cr)-LP exhibited regular octahedral crystals with an average diameter of about 100 nm, whereas high-angle annular dark-field scanning transmission electron microscopy and energy-dispersive X-ray spectroscopy confirmed that Cr, B, F, and N were homogeneously distributed in the octahedral crystals of MIL-101(Cr)-LP.

Ma and coworkers<sup>8</sup> went on to employ MIL-101(Cr)-LP as a catalyst for the reduction of imines by using H<sub>2</sub>. For example, *N*-benzylideneaniline, *N*-benzylidene-1-phenylmethanamine, and acridine were reduced in 38%, 100%, and 22% yields, respectively. Comparison with the analogous homogeneous FLP catalyst system revealed that the MOF-based catalyst exhibited selectivity for substrates where the substituent on N was less sterically demanding, whereby the MIL-101(Cr)-LP catalyst exhibited activity comparable to that of the homogeneous catalyst. Indeed, whereas the larger imine substrate *N*-benzhydryl-1-phenylmethanimine yielded 42% of the corresponding reduction product with the MOF-based catalyst, no product was obtained for the smaller substrate *N*-(diphenylmethylene)-1,1-diphenylmethanamine, even after 24 hr of reaction. These observations demonstrate that MIL-101(Cr)-LP is an active hydrogenation

that exhibits size selectivity due to the restricted access to the catalyst site imparted by the MOF structure.

In a similar fashion, the MOF-based catalyst also reduced alkylidene malonates, including diethyl 2-benzylidene-malonate, diethyl 2-hexylidenemalonate, diethyl 2-(2-methylpropylidene) malonate, and diethyl 2-(cyclohexylmethylene)malonate in 95%, 84%, 83%, and 88% yields, respectively. These yields were slightly higher than those derived from the parallel homogeneous FLP catalyst.

In addition, MIL-101(Cr)-LP was used to catalyze the hydroboration of the imine *N*-*tert*-butyl-1-phenylmethanimine with HBPIn. The observed reaction rate for the formation of the corresponding pinacolboramide was slower than that seen for the homogeneous FLP catalyst. The impact of LP loading in the MOF was also examined. Using MIL-101(Cr) with no LP resulted in no reduction, whereas use of MIL-101(Cr)-LP with 0.5, 0.75, and 1.00 mmol LP per 1 g MIL-101(Cr) gave 83%, 91%, and 100% pinacolboramide, respectively. The authors suggest a mechanism directly analogous to that proposed by Crudden and coworkers<sup>10</sup> for the homogeneous FLP catalyst. This was supported by *in situ* solid-state <sup>19</sup>F NMR spectroscopy of the reaction mixture, which provided evidence of [HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup>, an intermediate in the catalysis. The authors attribute the slower reaction rate to the necessary diffusion of substrates and products throughout the MOF pores.

The recyclability and long-term stability of MIL-101(Cr)-LP was probed. Indeed, NMR spectroscopic analysis of the supernatant after the reaction showed no evidence of leaching of the LP from the MOF. In addition, the recovered MIL-101(Cr)-LP was readily recycled and was shown to perform well upon re-use through seven cycles. As well, the recovered catalyst showed no evidence of degradation by <sup>1</sup>H NMR spectroscopy, PXRD, or N<sub>2</sub> adsorption studies.

In summary, Ma and coworkers<sup>8</sup> have established the first point of intersection of the ever-expanding area of MOF chemistry with the emerging field of main-group catalysis enabled by FLPs. The work reported in this issue of *Chem* illustrates that incorporation of such catalysts in a MOF offers the advantages of stability, recyclability, and selectivity. Although others have described efforts to develop heterogeneous FLP catalysts, this is the first effort that marries FLPs and MOFs for heterogeneous catalysis. This new paradigm offers enormous potential for further development given the range of FLP catalysts known and the huge variety of MOFs available. I believe the present advance described by Ma and coworkers will prove seminal and foreshadows a vast array of new stable, recyclable, and selective FLP catalysts embedded in MOFs.

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## Preview

# One Step Forward: A Novel “Step-Conjugated” Biphosphole

Jeffrey M. Lipshultz<sup>1</sup> and Alexander T. Radosevich<sup>1,\*</sup>

**New structural scaffolds for use in organic electronic materials are in high demand, especially if they possess unique optoelectronic or morphological properties. In this issue of *Chem*, Dobrovetsky, Baumgartner, and coworkers describe the synthesis of a new “step-conjugated” bi(dithienophosphole) and demonstrate its unique structural and electronic features.**

Fundamental discoveries in semiconducting  $\pi$ -conjugated organic molecular scaffolds are fueling an ongoing revolution in organic optoelectronics.<sup>1,2</sup> New applications for organic light-emitting diodes, organic field-effect transistors, and organic photovoltaic cells all rely on innovations in the design and preparation of conjugated molecules, especially those containing heteroaromatic subunits. As structure-function principles governing organic semiconductors have become better refined,<sup>3</sup> synthetic chemists with a practical knowledge of the main-group elements have found an opening. The fundamental trends in atomic character impart “heavy-element” p-block compounds with interesting properties that might not be immediately apparent from their periodic relationship with venerable first-row organic congeners. The situation is well illustrated in group 15; phosphole—the heavier analog of pyrrole—exhibits low aroma-

ticity arising from the high s-character in the lone pair on phosphorus, diminishing delocalization into the surrounding  $\pi$ -system and resulting in a nonplanar geometry.<sup>4</sup> Together, these effects impart differential electronic and photophysical properties to phospholes relative to other  $\pi$ -conjugated structures,<sup>5</sup> thus offering new possibilities for organic electronics.<sup>6</sup>

In this issue of *Chem*, Dobrovetsky, Baumgartner, and coworkers report the discovery of a previously unknown bi(dithienophosphole) scaffold with an interesting molecular and electronic architecture arising from a novel P–P bond-forming reaction between *P*-aminophospholes.<sup>7</sup> Baumgartner and coworkers had previously directed research toward *P*-aminophospholes as building blocks for the synthesis of varied phosphole derivatives,<sup>8</sup> but in their current work, Fortuna’s hand weighed heavily on the rudder, given that attempted

purification of *P*-amino-dithienophosphole **1** by column chromatography on alumina unexpectedly led to the precipitation of crystalline material. Surprisingly, single-crystal X-ray crystallographic analysis showed the product to be bi(dithienophosphole) **2** (Scheme 1A). The unanticipated formation of a P–P bond under these otherwise innocuous conditions clearly warranted further investigation.<sup>9</sup>

Positing that the mildly acidic chromatographic conditions might be responsible for the unintended dimerization reaction, the authors were able to confirm that reaction of the Lewis acid  $\text{BF}_3 \cdot \text{OEt}_2$  with *P*-aminophosphole **1** also yielded the biphosphole **2** (Scheme 1A). However, resolving the issue of *why* bi(dithienophosphole) **2** formed did not address the issue of *how* it was happening—what is the precise role of the acid in facilitating the dimerization? *In situ* spectroscopic investigations of the reaction of *P*-aminophosphole **1** with  $\text{BF}_3 \cdot \text{OEt}_2$  provided a clue. <sup>31</sup>P NMR spectra showed a set of doublet resonances with large, complementary coupling constants—telltale signs indicating the formation of an unsymmetrical P–P bond. Through correlated heteronuclear (<sup>1</sup>H and <sup>31</sup>P) NMR spectra, it was further established that the unsymmetrical intermediate possessed a single pyrrolidinyl

<sup>1</sup>Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

\*Correspondence: [radosevich@mit.edu](mailto:radosevich@mit.edu)  
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