

A Meeting of Metals—A Joint Virtual Issue between *Organometallics* and *ACS Catalysis* on First-Row Transition Metal Complexes

Organometallic and catalytic chemistry are two of the most vibrant, impactful, and transformative fields in chemistry. Transformations enabled by this intersection impact drug discovery, alternative energy schemes, and materials synthesis to name but a few. Some of the most successful and prominent catalysts are ones that contain transition metal complexes; hence, there is a natural synergy between these two overlapping fields. It is therefore timely that the leading ACS publications in these areas, *Organometallics* and *ACS Catalysis*, organize a joint virtual issue to highlight some of the new exciting chemistry at the intersection of catalysis and compounds containing metal–carbon bonds. This effort not only highlights some great science but also reinforces the partnership between prominent titles in the ACS portfolio.

In particular, the topic of this first virtual issue highlights the resurgent area of catalysis and organometallic chemistry with first-row transition metals. Organometallic chemistry has its roots in compounds of manganese, iron, cobalt, nickel and copper. Traditionally, these molecules featured strong-field ligands and were in most cases high in electron count; coordinatively saturated; and hence, frequently did not exhibit catalytic activity. Creative and insightful ligand design has been used to stabilize low-coordinate iron and cobalt compounds and open new pathways for reactivity and, in some cases, catalysis. *Organometallics* articles in this Virtual Issue from Deng, Danopoulos, García and a communication from Jones et al. highlight how N-heterocyclic carbenes, phosphines and amides, some of the most widely studied ligand types, find application in new chemistry of earth abundant transition metals. Contributions from Linehan and Appel, Bryliakov, and Chang and co-workers in *ACS Catalysis* demonstrate the use of classic chelating phosphine, salalen, and cyclopentadienyl ligands to coax new chemistry from Co and Ti catalysts for carbon dioxide hydrogenation, enantioselective oxidations, and C–H functionalization reactions. Pincer ligands, meridionally coordinating tridentate chelates, continue to attract considerable interest from both the synthetic organometallic and homogeneous catalysis communities. Therefore, it is not surprising that pincer chemistry is prominently featured in our joint Virtual Issue. Articles from Chirik, Fout and Kirchner explore the fundamental organometallic chemistry of cobalt and nickel complexes relevant to C–H functionalization and cross-coupling, which are some of the most prominent catalytic reactions typically in the realm of precious metal catalysis. Two contributions from Xile Hu's group report the application of iron pincer complexes in hydrogenation and Kumada-type cross-coupling chemistry. Pincer ligands that support Fe catalysts are also featured in *ACS Catalysis* contributions. Cariou and Shabaker report a unique tandem catalytic ethylene oligomerization that uses two Fe catalysts, one supported by a pyridyl-diimine ligand. Methanol is a possible target for hydrogen storage, but this requires facile removal of hydrogen. Bernskoetter, Hazari, Holthausen and co-workers report on the use of PNP-ligated Fe catalysts for methanol dehydrogenation

with turnovers >50 000. Finally, Szymczak and co-workers have developed an iron catalyst for alkene hydroboration. Here, the secondary coordination sphere of a meridionally coordinated *N,N,N*-ligand is used to modulate the catalyst's activity and selectivity.

Although catalyst modulation using sophisticated ligand design is often beneficial, sometimes relatively simple catalysts for important reactions can be realized. For example, Garg and co-workers have developed catalytic amination of aryl *O*-sulfamates and chlorides using commercially available NiCl₂(dimethoxyethane). The method has been demonstrated for a broad substrate scope and is tolerant of many substituents.

One can observe a clear distinction of how electrons flow and redox couples are accessed in catalytic cycles when considering first-row transition metals in comparison with their second- and third-row counterparts. A contribution from Rauchfuss and co-workers demonstrates cooperative electron flow between the supporting ligands and iron and its role in catalysis. An article from Kubiak and Walensky compares the performance of isoelectronic α -diimine manganese and rhenium carbonyl complexes in the electrocatalytic reduction of CO₂, one of the most prominent catalyses in contemporary catalytic chemistry. Along these lines, García and co-workers report the application of carbon dioxide reduction with silanes as the carbon source for the methylation of amines using nickel phosphine complexes. Solar-driven production of hydrogen from water is among the most important and challenging chemical reactions. In another featured manuscript, Eisenberg, Holland, and co-workers focused on new energy processes, and showed the utility of Ni(II) catalysts for light-driven production of hydrogen from water.

Catalytic functionalization of C–H bonds has been a long-standing goal and focus of both the organometallic and catalysis communities. Historically, second- and third-row transition metals have held a privileged position in the field of C–H activation and, more recently, catalytic C–H functionalization. However, in recent years, substantial progress has been made developing C–H functionalization reactions using catalysts based on first-row transition metals. For example, Ackermann and Ma have developed a Co-catalyzed synthesis of isoindolinone derivatives via C–H alkenylation reactions. These oxidative amination reactions permit the efficient annulation of electron-deficient alkenes by benzamides. In addition, Huang and co-workers have developed regioselective C–H benzylation of enones with toluenes via radical-triggered oxidative coupling using a Cu(II) catalyst. The reaction is versatile, and 27 examples with up to 98% yield have been disclosed.

Computational modeling continues to play an increasingly important role in the understanding of organometallic and catalytic reactions. This includes efforts to understand

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mechanistic details as well as to rationally design new classes of reactions and catalytic processes. Two contributions from *ACS Catalysis* highlight recent advances based on computational modeling. Relevant to the contribution from Kubiak and Walensky (see above), Nielsen, Gray, Goddard, and Lam have disclosed a DFT study of Mn catalysts for electrocatalytic reduction of carbon dioxide. Such studies are critical to developing a detailed understanding of the mechanism of catalysis. In another study, Liu and Yang used DFT to probe the mechanism of ortho C–H cyanation of vinylarenes using a Cu catalyst. The calculations revealed a Cu-catalyzed electrophilic cyanative dearomatization, followed by base-catalyzed hydrogen transposition.

No doubt there were more articles worthy of a highlight, and hopefully more are to come, but for now, we invite you to take a look pubs.acs.org/page/vi/2015/tm_complexes and become reacquainted with *the* “first row”, which is changing our thinking.

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Notes

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