Development of Organometallic Catalysts for Greener Methanol Carbonylation

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Millions of tons of "acetyls" such as acetic acid and acetic anhydride are produced each year, before these basic building blocks of chemical industry are elaborated into esters, amides, and eventually polymer materials, pharmaceuticals, and other consumer products. The vast majority of acetyls are produced industrially through homogeneous catalysis that relies on toxic methyl iodide promotors and scare precious metal catalyst. Therefore, development of iodide-free processes and/or earth-abundant catalysts has attracted the attention of both academic and industrial scientists.

In the first part, fundamental studies on C–O bond activation using iridium complexes will be presented as a new direction for iodide-free carbonylation. The C–O cleavage of ether and ester was discovered using iridium(I) pincer complexes. The individual steps of methanol carbonylation to methyl acetate was studied to demonstrate an alternative approach for iodide-free carbonylation. Mechanistic studies show initial C–H activation and carbene formation by iridium(I) species to precede productive C–O bond activation. Kinetic studies of migratory insertion and reductive elimination reveal essential roles of the solvent methanol and distinct features of acetate and iodide anions that are relevant to the design of future catalysts for iodide-free carbonylation.

In the second part, nickel catalyst for ester carbonylation will be presented. The nickel catalysts supported by N-heterocyclic carbene ligands mediate the carbonylation of methyl esters producing anhydrides with high yields at low catalyst loading. The use of persistent carbene supporting ligands, which can be added as their air-stable imidazolium salt conjugate acid form, represents a dramatic improvement over prior nickel-catalyzed carbonylation reactions supported by tertiary phosphine ligands, raising hopes for industrial application of base metal carbonylation catalysts.