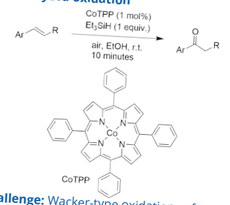
Homogeneous Catalysis Papers of the Month

December 2023

non-PGM catalysis

Co-catalyzed oxidation

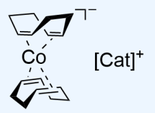


Challenge: Wacker-type oxidations often use less sustainable and and more expensive palladium catalysts.

Solution: : Markovnikov-selective oxidation of olefins can be catalyzed by a cobalt-tetraphenylporphyrin complex under ambient conditions, providing broad functional group tolerance.

N. Abuhafez et al., *Angew. Chem. Int. Ed.* **2023**, doi: 10.1002/anie.202316825

Counterions in Co catalysis

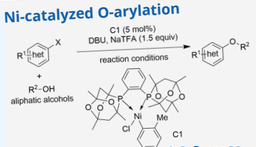


Challenge: The counterion sensitivity of transition-metal-catalyzed alkene hydrogenation has rarely been investigated.

Solution: The precatalyst $[Co(\eta^4\text{-cod})_2]^-$ was found to be most effective with magnesium or lithium countercations when hydrogenating highly-substituted alkenes.

M. Gawron et al., *Angew. Chem. Int. Ed.* **2023**, doi: 10.1002/anie.202315381

Ni-catalyzed O-arylation



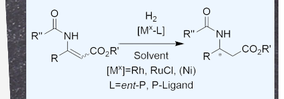
Challenge: Ni-catalyzed C-O cross-coupling uses inorganic bases, which are poorly soluble and often cause reaction issues.

Solution: O-arylation of aliphatic alcohols and phenols is catalyzed by PAd_2-DalPhos/Ni in the presence of organic bases DBU or BTPP, producing a wide range of (hetero)aryl ethers.

K. M. Morrison et al., *ACS Catal.* **2023**, doi: 10.1021/acscatal.3c05405

Review

β-amido acrylate hydrogenation



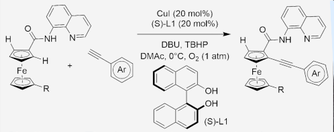
Challenge: Enantiomeric phosphine ligands are widely used in the hydrogenation of β-amido β-substituted acrylates, and isomers often react differently.

Solution: A comprehensive review of β-amido acrylate hydrogenation evaluates catalyst systems, including ligands, metals, reaction conditions, and enantioselectivities.

M. Stephan et al., *Org. Process Res. Dev.* **2023**, doi: 10.1021/acs.oprd.3c00333

C-H functionalization

Enantioselective C-H activation

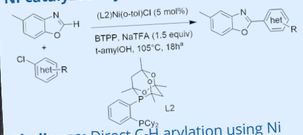


Challenge: The inner-sphere mechanism of copper-catalyzed C-H activation has not been well-developed, and often requires high temperatures and results in low selectivities.

Solution: A Cu/BINOL-catalyzed C-H alkynylation has been developed, requiring only mild conditions and providing good yields (77%) and high enantioselectivities (94% ee).

Z.-Z. Zhang et al., *ChemRxiv* **2023**, doi: 10.26434/chemrxiv-2023-n1wv0

Ni-catalyzed arylation

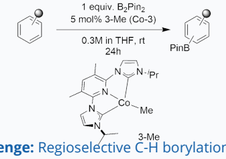


Challenge: Direct C-H arylation using Ni often requires high loadings of expensive or air-sensitive reagents and catalysts.

Solution: An air-stable precatalyst system of Ni(II) and CyPAd-DalPhos or PhPAd-DalPhos combines with BTPP/NaTFA to allow cross-couplings between (hetero)aryl (pseudo)halides and azoles.

N. E. Bode al., *Org. Lett* **2023**, DOI: 10.1021/acs.orglett.3c03393

Co-catalyzed borylation



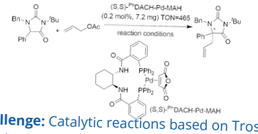
Challenge: Regioselective C-H borylation usually relies on directing groups or steric effects, which leads to difficulty when using weakly coordinating substituents such as fluorine.

Solution: Remote C-H activation and borylation is catalyzed by Co with N-alkyl-imidazole–substituted pyridine dicarbene pincer ligands, showing a kinetic preference for meta sites.

J. B. Roque et al., *Science* **2023**, doi: 10.1126/science.adj6527

New catalyst

Pd-catalyzed alkylation



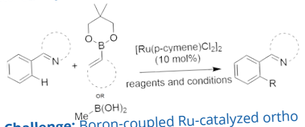
Challenge: Catalytic reactions based on Trost-type ligands require a large amount of precatalyst and ligand, and often inefficient activation strategies.

Solution: Single-component, bench-stable, easily activated Trost-type and PHOX-type chiral precatalysts were developed for Pd(0) asymmetric alkylation, providing high reactivity at low loading.

J. Huang et al., *Nature Commun.* **2023**, doi: 10.1038/s41467-023-43512-8

Electrochemistry

Ru-catalyzed ortho functionalization

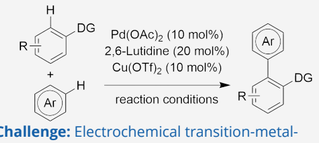


Challenge: Boron-coupled Ru-catalyzed ortho functionalization has been less explored than electrophile-coupled reactions.

Solution: Electrochemical oxidation and catalysis by $[Ru(p\text{-cymene})Cl_2]_2$ allows ortho-directed functionalization using boronic esters as coupling partners.

J. Kenyon et al., *Adv. Synth. Catal.* **2023**, doi: 10.1002/adsc.202301184

Pd-catalyzed arylation



Challenge: Electrochemical transition-metal-catalyzed cross-dehydrogenation is not well understood mechanistically.

Solution: Pd-electrocatalyzed oxidative coupling shows evidence that the turnover limiting step is transmetalation between two organopalladium complexes.

Z. Lin et al., *J. Am. Chem. Soc.* **2023**, doi: 10.1021/jacs.3c08479

Selected papers from the catalysis literature published online in December 2023 (including pre-prints)

SINOCOMPOUND
Accelerate to the next phase