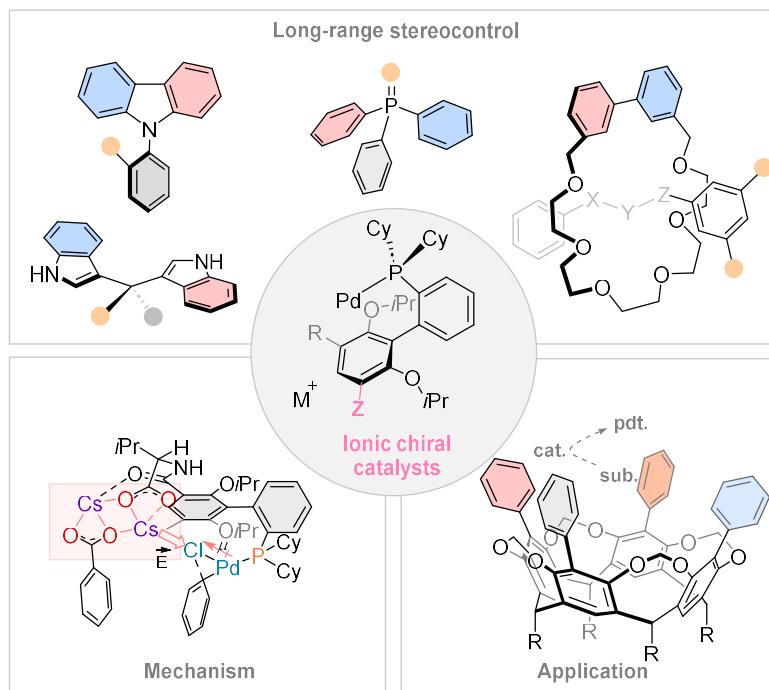


Electrostatic interactions enable remote stereocontrol in palladium-catalyzed cross-coupling

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Incorporating ionic groups into synthetic transition-metal catalysts represents a promising design element for enantioselective reactions. However, the nondirectional nature of ionic interactions presents a unique challenge in the precise transmission of chirality from the catalysts to the prochiral substrates. In this talk, I will present our recent work on innovating three generations of phosphine ligands possessing nonligating ionic groups to exert long-range stereocontrol in Pd-catalyzed cross-coupling reactions. The applications of the ionic ligand–substrate interaction strategy in enantiotopic-group-selective reactions and atroposelective reactions to access quaternary carbon, triaryl phosphorus, axial biaryls, mechanically planar chiral rotaxanes, and inherently chiral cavitands will be discussed to illustrate the synthetic utilities. In addition, experimental and computational mechanistic studies reveal unconventional combinations of electrostatic steering and electrostatic catalysis by the oriented internal electric field produced by the ionic ligand–substrate interactions.



Scheme 1. Asymmetric catalysis enabled by distal ionic ligand–substrate interactions

References

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