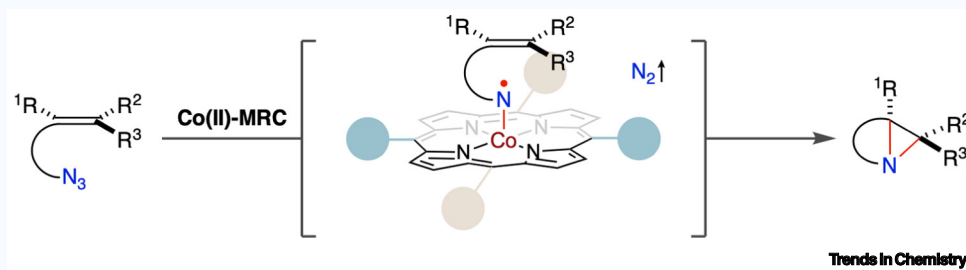


Asymmetric radical aziridination of alkenes

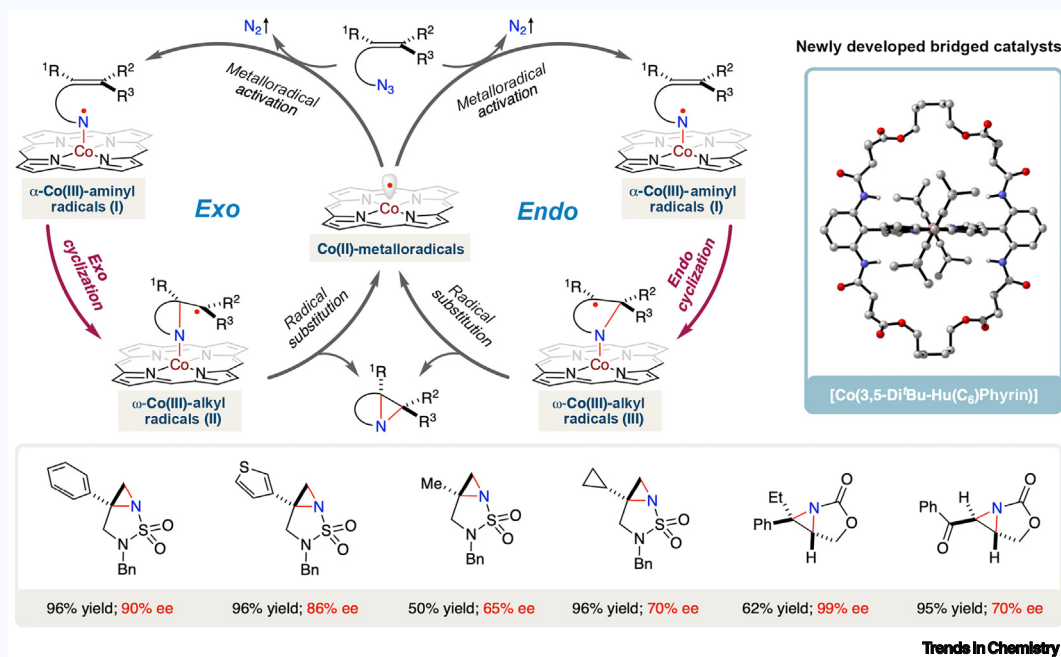
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ORIGIN

Metalloradical catalysis (MRC) exploits metal-centered radicals from open-shell metal complexes as one-electron catalysts for homolytic activation of substrates, generating metal-entangled organic radicals that serve as pivotal intermediates to direct the reaction pathway and stereochemical outcome of catalytic radical processes. Building on established intermolecular olefin aziridination with organic azides, recent advances have led to the development of Co(II)-based metalloradical systems that enable asymmetric *N*-heterobicyclization via a stepwise radical mechanism.

REACTION MECHANISM

Cobalt(II) complexes of porphyrins, which belong to the category of stable 15e-metalloradicals, have proved their efficacy as catalysts for the radical bicyclization of organic azides. Supported by *D*₂-symmetric chiral amidoporphyrin ligands offering tunable steric, electronic, and chiral environments, the Co(II)-based metalloradical system provides a general approach for efficient construction of highly strained chiral bicyclic aziridines with effective control over stereoselectivities. The Co(II) porphyrin complexes display a remarkable capability for homolytic activation of diverse organic azides, generating the corresponding α-Co(III)-aminyl radicals **I**. This process involves translocation of the radical character from the catalyst's metal center to the α-nitrogen atom of the azide metalloradicalophile, concurrently releasing dinitrogen gas. The initially generated α-Co(III)-aminyl radicals **I** may undergo either *exo*- or *endo*-cyclization, leading to the formation of the respective ω-Co(III)-alkyl radicals (**II** or **III**) while forming the first C–N bond. The resulting ω-Co(III)-alkyl radicals (**II** or **III**) effectively engage in intramolecular radical substitution, forming the second C–N bond and breaking the weak Co–N bond while simultaneously regenerating the Co(II)-based metalloradical catalysts. The regioselectivity in the radical addition (*exo*- vs *endo*-cyclization) of intermediate **I** plays a crucial role in determining the mode of asymmetric induction and influencing the control of stereochemistry during catalysis. Owing to its distinctive stepwise radical mechanism, Co(II)-catalyzed bicyclization offers the opportunity to accommodate a broad range of organic azides bearing dangling alkene units. Notably, the substrates containing electron-deficient alkene units, which are typically challenging in catalytic systems involving electrophilic metallonitrene intermediates, can be effectively aziridinated by the Co(II)-based metalloradical system.



IMPORTANCE

Distinct from existing catalytic systems via a concerted mechanism involving electrophilic metallonitrenes, intramolecular aziridination by Co(II)-metalloradicals follows a stepwise radical pathway that engages two metal-entangled organic radicals: α-Co(III)-aminyl radicals and ω-Co(III)-alkyl radicals. Besides its fundamental significance, Co(II)-catalyzed radical bicyclization presents an attractive method for the stereoselective synthesis of valuable chiral bicyclic aziridines from diverse organic azides while generating dinitrogen as the sole byproduct.

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Declaration of interests

The authors declare no competing interests.

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