

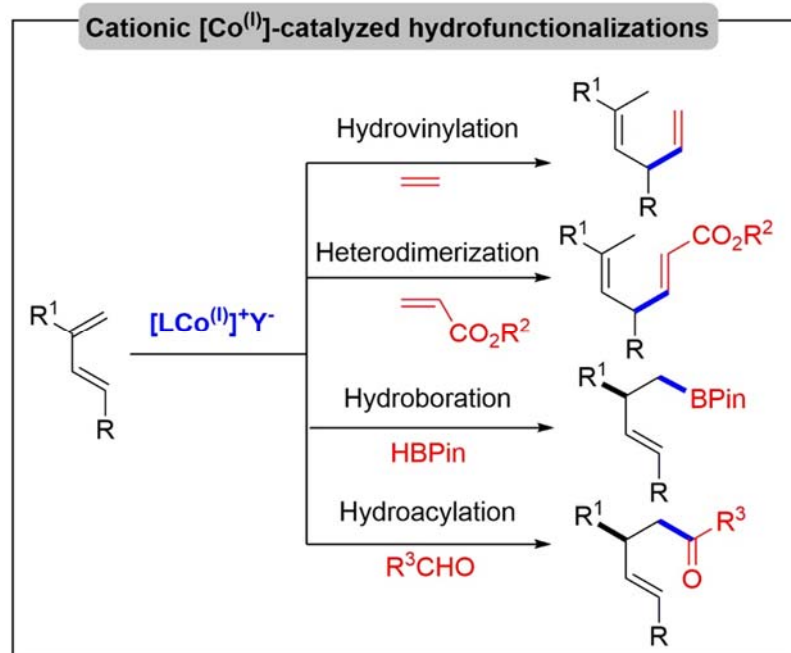
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Cationic cobalt(I) intermediates in hydrofunctionalization reactions

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Discovery of base metal-catalyzed methods for the preparation of chiral intermediates has garnered great attention. Recently, through a systematic study of activators and ligands, we have discovered Co(I)-catalyzed enantioselective heterodimerization of linear 1,3-dienes with ethylene and acrylates. In these studies, cationic cobalt(I) has been invoked as an active catalyst to carry out the transformation. However, the synthesis and isolation of such active Co(I)-complexes which could give insight into of reaction's mechanism, remains challenging. Herein, we disclosed a reliable procedure for the synthesis and isolation of Co(I)-complexes and characterized them by UV-Vis spectroscopy and X-ray crystallography. The *bis*-phosphine ligated Co(I) complexes in presence of activators, performed the regio- and enantioselective hydroboration of 2-substituted 1,3-diene with pinacolborane (HBPin) to obtain homoallylic boronates (enantiomeric excess, *ee* >90%). In the absence of activators, these complexes *do not catalyze* the reaction suggesting the key role of cationic Co(I)-species in the catalytic cycle. Currently, these Co(I) complexes are being further utilized in the hydroacylation of 1,3-dienes with simple aliphatic aldehyde to produce enantiopure ketones. The comprehensive protocols for the synthesis of Co(I) complexes and its application in hydrovinylation, heterodimerization with acrylates, hydroboration, and hydroacylation of 1,3-dienes will be discussed.



Cationic Co(I)-catalyzed hydrofunctionalization reactions