Dehydrocoupling of Phosphines with Nickel Complexes: Ligand effects on Product Selectivity

Abstract

Dehydrocoupling is a chemical reaction that forms main group element-element σ bonds between molecules and releases hydrogen gas as a byproduct. Dehydrocoupling is an effective tool in the formation of inorganic polymers with unique electronic properties. The bisphosphinite pincer-ligated nickel complex (POCOP)NiMe (POCOP) = 2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$ dehydrocouples primary and secondary phosphines catalytically. However, this catalyst is unselective and generates a large product distribution of known and unknown phosphorus-containing products. It was hypothesized that the alkyl groups on the phosphine component of the ligand sterically and electronically effect substrate coordination to the metal center. The nature of the phosphine component influence the ability of substrates to approach nickel (sterics) and the bond energies at nickel (electronics). These effect thus influence the products generated. To test these effects, a series of bidentate pincer-ligated nickel complexes (POCOP)NiMe, (POCOP) = 2,6-(R$_2$PO)$_2$C$_6$H$_3$ (R = ^{t}Bu, ^{n}Bu, Me, Ph) were synthesized and used in the catalytic dehydrocoupling of primary and secondary phosphines to probe the ligand influences on the distribution of dehydrocoupled products.