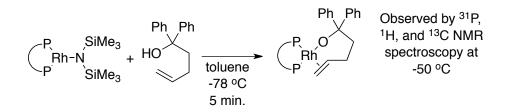
The Effects of Ancillary Ligand Properties on the Reactions of Rhodium Diphosphine Alkoxo Alkene Complexes

Dipnospnine Alkoxo Alkene Complexes		
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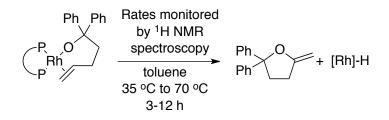
Rhodium diphosphine alkoxo alkene complexes were synthesized by the addition of unsaturated alcohols to rhodium diphosphine silylamido complexes at -78 °C (

Scheme 1). The alkoxo alkene complexes were characterized by NMR spectroscopy at 50 °C and allowed to react at either 35 °C or 70 °C. The reactions produced tetrahydrofurans and rhodium hydrido complexes by a mechanism involving alkene insertion into the rhodium alkoxo bond and β -hydrogen elimination (

Scheme 2). The reactions were monitored by ¹H NMR spectroscopy, and the rate constants for insertion of the alkene ligand into the alkoxo ligand were determined by fitting the exponential curves to the data. The effects of the ancillary ligand on the rates for alkene insertion were determined by systematically varying the electronic, steric, and bite angle properties of the diphosphine ligand and observing how these changes affect the rates for alkoxo alkene complex decomposition and furan formation. The data show that the properties of the ancillary ligand do affect the rates for alkene insertion into rhodium-alkoxo bonds, and that certain characteristics or properties are desirable for promoting this reaction.



Scheme 1: Syntheses of rhodium diphosphine alkoxo alkene complexes



Scheme 2: Reactions of rhodium diphosphine alkoxo alkene complexes.

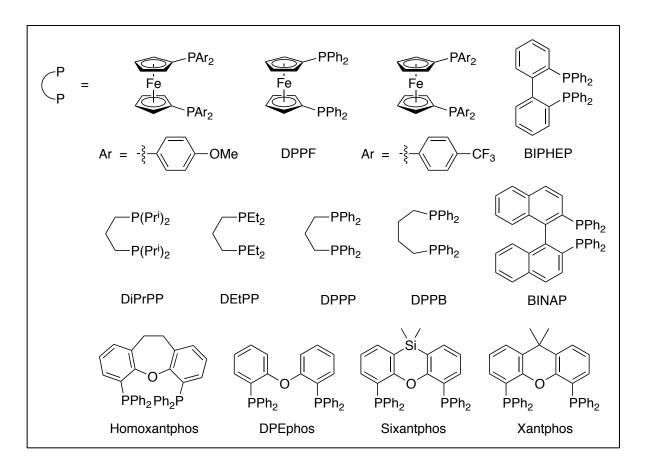


Figure 1: Diphosphines investigated.