

Abstract

This Thesis describes the synthesis, reactivity, coordination properties, and catalytic activity of novel electronically dissymmetric bisphosphines structurally related to 1,1'-bis(diphenylphosphino)ferrocene (dppf).

First, a methylene spaced congener containing a primary phosphine group, which is stable in the air, $\text{Ph}_2\text{PfcCH}_2\text{PH}_2$ (fc = ferrocene-1,1'-diyl), was prepared. While studying its reactivity, an unprecedented stable primary phosphine oxide, $\text{Ph}_2\text{PfcCH}_2\text{P}(\text{O})\text{H}_2$, was isolated. The primary phosphine, the corresponding phosphine oxide, dppf and the known bis-tertiary phosphine $\text{Ph}_2\text{PfcCH}_2\text{PPh}_2$ were studied as ligands in Ru(II) complexes. The catalytic activity of the defined complexes was compared in two ruthenium-catalyzed reactions: cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran and isomerization of estragole to anethole.

Second, the remarkable stability of the prepared primary phosphine oxide called for a detailed investigation of this poorly described class of compounds. As a result, stable primary phosphine chalcogenides lacking steric protection $\text{FcCH}_2\text{P}(\text{Y})\text{H}_2$ (Fc = ferrocenyl; Y = O, S, Se) were isolated for the first time. These compounds were studied as ligands in reactions with hard and soft Lewis acids (Zn(II) and Ru(II)), and the reactivity of the P-H hydrogens was examined via reactions with various unsaturated substrates (RCHO, R_2CO , PhNCE; R = Me, Ph; E = O, S).

Subsequently, $\text{Ph}_2\text{PfcCH}_2\text{PH}_2$ was employed in acid-catalysed condensation reaction with acetylacetone to produce the bulky bisphosphine $\text{Ph}_2\text{PfcCH}_2\text{PCg}$ (PCg = 1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphaadamantyl). Together with Ph_2PfcPCg , these bisphosphine ligands were used to prepare defined Pd(0) and Pd(II) complexes, and tested in selected catalytic reactions compared to their analogs derived from dppf. Specifically, the Pd(0) complexes were applied to C-H arylation of benzoxazoles with aryl chlorides, in which they showed excellent catalytic activity and selectivity. Conversely, the Pd(II) complexes were employed in cyanation of aryl bromides using $\text{K}_4[\text{Fe}(\text{CN})_6]$ as a non-toxic cyanide source and in the Suzuki-Miyaura reaction of benzoyl chlorides with arylboronic acids to give benzophenones.

Last but not least, a new polar bidentate ligand $\text{Ph}_2\text{PfcPO}_3\text{H}_2$ was prepared by hydrolysis of the corresponding ethyl ester. However, although the ligand, its ammonium salts, and even Pd(II) complexes were prepared and fully characterized, they gradually decomposed upon storage, which prevented further studies into the catalytic properties of these compounds.

Keywords: *bisphosphines, ferrocene ligands, homogeneous catalysis, primary phosphine chalcogenides, phosphonic acid.*