

Abstract

The first part of this Thesis describes the preparation of a novel phosphanyl-ferrocene amine, $\text{Ph}_2\text{PfcCH}_2\text{NH}_2$ (**1**; fc = 1,1'-ferrocendiyl) in two steps from the known aldehyde Ph_2PfcCHO . An oxime $\text{Ph}_2\text{PfcCH}=\text{NHOH}$ was prepared firstly by a condensation reaction, and subsequently treated with $\text{Li}[\text{AlH}_4]$ to give the desired amine. The amine was converted into its more stable hydrochloride salt, $\text{Ph}_2\text{PfcCH}_2\text{NH}_3\text{Cl}$.

Derivatization of amine **1** was examined through the preparation of a series of phosphanyl-urea ligands $\text{Ph}_2\text{PfcCH}_2\text{NHC(E)NR}^1\text{R}^2$. Some of these compounds were also prepared via an alternative method employing reductive amination reaction. These donors and their Pd(II) complexes were evaluated in Pd-catalyzed reaction of arylbromides with $\text{K}_4[\text{Fe}(\text{CN})_6]$ in order to prepare corresponding benzonitrile derivatives using aqueous reaction solvents. The reaction proceeds with excellent yields and purity when 1 mol.% of Pd-catalyst is used (at 100 °C for 3 hours), especially for electron-rich bromobenzenes. Substrates with electron-withdrawing substituents react significantly slower and corresponding hydrolytic products (benzamides) are isolated.

The coordination properties of phosphanyl-amine **1** were examined towards Cu(I) ions. Thus, reaction of **1** with $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$ provided bis-chelate complex $[\text{Cu}(\mathbf{1}-\kappa^2\text{N},\text{P})_2][\text{BF}_4]$, which was also studied electrochemically. A similar reaction with CuCl furnished a few crystals of an unexpected mixed-valence Cu(I)/Cu(II) octacopper complex $[\text{Cu}_4\{\mu(\text{P},\text{N})\text{-}\mathbf{1}\}_2(\mu\text{-Cl})_5\text{Cl}(\mathbf{1H}\text{-}\kappa\text{P})(\text{H}_2\text{O})_2]$. Both complexes were studied by X-ray diffraction.

The second part of this Thesis describes the preparation of Ph_2PfcCN (**2**) from aforementioned oxime $\text{Ph}_2\text{PfcCH}=\text{NHOH}$. Phosphanylnitrile was utilized in an extensive coordination study towards Group 11 metal cations. A significant influence of the anion on the structure of the produced complex was observed and several new and unprecedented coordination geometries were disclosed. Among the obtained compounds, gold(I) complexes proved to be highly efficient catalysts for gold-mediated catalyzed isomerization of (*Z*)-3-methylpent-2-en-4-yn-1-ol and oxidative [2+1+2] cycloaddition of acetylenes, *N*-oxides and nitriles. Both of these reactions were used for the preparation of natural compounds, rosefurane and annuloline.

Keywords: ferrocene; ferrocene ligands; phosphanylurea; phosphanylnitrile ligands; coordination study; structural analysis; Pd-catalysis; Au catalysis.