CATALYTIC FORMATION OF C-S BONDS

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Our recent research interests focus on development of homogeneously catalyzed reactions for the synthesis and use of sulfur-containing compounds, such as thioethers. They constitute valuable target compounds for material science and pharmaceutical applications [1]. Herein, two conceptually different synthetic methodologies for their construction will be presented.

We have developed a general Ni-catalyzed coupling of challenging aryl chlorides and \textit{in situ} generated aliphatic and aromatic thiola tes [2]. Well-defined and air-stable Ni precatalysts were used to transform a broad scope of substrates containing various functional groups and heterocyclic motifs.

Moreover, a Pd-catalyzed tandem isomerizing hydrothiolation of 3-arylpropenes was investigated [3]. The catalyst system consisting of a Pd(II) precursor, bidentate phosphine ligand and strong Bronsted acid was able to convert a variety of substrates to branched benzylic thioethers in a highly regioselective manner.

\[ \text{C-S Coupling} \]

\[ \begin{array}{c}
\text{R-Cl} \\
\text{[Ni]} \\
\text{R'SH} \\
\rightarrow \\
\text{R-SR'}
\end{array} \]

\[ \text{Isomerizing Hydrothiolation} \]

\[ \begin{array}{c}
\text{Ar-} \\
\text{[Pd]} \\
\text{R'SH} \\
\rightarrow \\
\text{Ar-SR'}
\end{array} \]