Abstract

This dissertation describes the synthesis of phosphane functionalized imidazolium salts and their use in the preparation of chelating mixed phoshane carbene ligands. The novel ligands were used for the synthesis of homoleptic complexes of Rh(I), Ir(I), Ni(II) and Pd(II). The reactivity of the Rh(I) and Ir(I) complexes with respect to small molecules has been investigated and the catalytic activity of the Pd(II) complexes for *Suzuki* coupling has been explored as well.

Starting from ethylvinylimidazolium iodide and $HPPh_2$ the imidazolium ligand precursors **E5** and **E6** were synthesized in high yield. Their conversion to the aspired mixed phoshane carbene ligand **E7** has been accomplished in situ by deprotonation with $K[N(SiMe_3)_2]$. The degree of conversion was almost quantitative as the reaction of the resulting solutions with CS_2 giving the thiocarboxylate **E8** proved.

In situ generated **E7** reacts with 0.5 equivalents $[Rh(\mu\text{-}Cl)(COD)]_2$ to give the novel homoleptic Rh(I) complexes *cis*-**E10**, *trans*-**E12,** *cis*-**E11**, *trans*-**E13** in high yields. All new complexes have been structurally characterized by single crystal X-ray crystallography. NMR spectroscopic stuidies of the dynamic behaviour of the complexes in solution have proved interconversion of *cis*- and *trans*-isomer at elevated temperatures. A mechanism for this reaction has been proposed.

The oxidative addition of small molecules like O_2, S_8, CH_3I, I_2 to *cis*-Rh(I) complexes **E10** or **E11**, respectively, afforded novel Rh(III) complexes **E14**, **E15**, **E16**, **E17**, **E19**. All new complexes have been characterized by standard spectroscopic methods and single crystal X-ray analysis. The complicated solution dynamics of the *cis*-peroxo-Rh(III) complex **E14** was explored in detail by ^{31}P NMR-spectroscopy. The synthesis of novel *cis*-Ir(I) complex **E20** has been achieved by reaction of **E7** with $[Ir(\mu\text{-}Cl)(COD)]_2$. It reacts with H_2, O_2, S_8, CO, CH_3I, I_2 giving the novel Ir(III) complexes, **E21**, **E22**, **E23**, **E24**, **E25, E26**. Their structures are described in detail. The synthesis of novel homoleptic *trans*-Ni(II) and Pd(II) complexes**,** **E27**, **E28** and their structural spectroscopic properties is described as well. The interconversion between *cis* and *trans* isomers of Pd(II) complex **E28** at high temperature was again proved by ^{31}P NMR spectroscopy. The catalytic activity of *trans*-Pd(II) complex **E28** with respect to *Suzuki* coupling was surveyed.