

Abstract

The subject of the presented work is the synthesis of mononuclear square-planar [(R-PyMA)Ni(Aryl)X]-type organonickel complexes with *N*-(Pyridin-2-yl-methylene)aniline-ligands (R-PyMA) and the investigation of their structure, reactivity and electrochemistry.

Single crystal X-ray diffraction showed the crystallisation of the *cis*-isomer, in which the halide ligand (X) is located opposite to the pyridine part of the PyMA-ligand, to be favoured over the *trans*-isomer. Furthermore a shift of the *cis*-/*trans*-ratio towards the *trans*-isomer could be observed at low temperatures using variable temperature NMR-spectroscopy.

The electronic character of the R-PyMA ligands with various substituents was determined through DFT-calculations using a [Ir(allyl)(CO)(R-PyMA)]-type model complex. The assessment of the electronic properties reveals that the donor strength of the unsymmetric PyMA ligands lies between the values for the structurally similar ligands 2,2'-bipyridine and *N,N*-bisphenyl-1,4-diazabutadiene. Additionally, the difference in Gibbs free energy ΔG between both isomers and the transition state for the isomerisation *via* the lowest energy pathway was determined. This transition state is a trigonal-planar arrangement, which is formed through decoordination of the halide ligand.

Spectroelectrochemical investigations of the complexes showed the formation of a [(R-PyMA)Ni(Aryl)(Solv)][•]-radical species from all [(R-PyMA)Ni(Aryl)X]-type complexes upon reduction and cleavage of the halide ligand. The required reduction potentials for all complexes lie between -1.2 and -1.8 V (vs. ferrocene/ferrocenium) and shift to less negative potentials for electron-rich R-PyMA ligands. The cleavage of the halide ligand, which leads to catalytic activation of the complexes, can be promoted by variation of the halide ligand itself following the series $F > Cl > Br > I$, as well as by using less electron-rich aryl-ligands. The latter increases the tendency for the transmetallation reaction of two [(R-PyMA)Ni(Aryl)X] complexes leading to the formation of [(R-PyMA)Ni(Aryl)₂] bisaryl-complexes.

Further reduction of these species was proven to take place in dimers formed from two of the [(R-PyMA)Ni(Aryl)(Solv)][•] radical complexes.