

Abstract

In this work, a number of substituted ethanolamines and ethylenediamine ligands were reacted with palladium, copper and titanium compounds to develop a new class of molecular complexes of the mentioned metals. For this purpose, 2-Methoxyethylamine (MOEA), 2-Pentafluorophenoxyethaneamine (POEA), *N*-Pentafluorophenylaminoethanol (PAEt), *N*-Pentafluorophenylethane-1,2-diamine (PEA) and *N,N'*-Bis(pentafluorophenyl)ethane-1,2-diamine (BPEA) were applied. MOEA and POEA were found to coordinate via the nitrogen atoms of their primary amino functions to form *trans*-[Pd(MOEA)₂X₂] (X = Cl, Br), *trans*-[Pd(POEA)₂Cl₂] and [Cu(POEA)₂Cl₂] derivatives. In the reaction between PAEt and PdCl₂ the complex *trans*-[Pd(PAEt)₂Cl₂] was obtained in which PAEt units were found to coordinate through their nitrogen atoms. The reaction of PAEt with copper(II) chloride led to the formation of the dimer [(PAEt)CuCl(μ-Cl)]₂ with PAEt acting as a bidentate ligand. A further coordination mode of PAEt was observed in the reaction of PAEt with [Ti(OPr^{*i*})₄] yielding the binuclear complex [Ti(HOPr^{*i*})(OPr^{*i*})₃(μ-O-PAEtat)]₂. Upon variation of the stoichiometry of PEA and COD palladium dihalides, various species of controllable composition were obtained. The palladium complexes [(PEA)PdX₂], *trans*-[Pd(PEA)₂Cl₂] and [Pd(PEA)₄]X₂ (X = Cl, Br) were isolated and structurally characterized, which allowed to postulate the mechanism to be a stepwise ligand exchange. Attempts to synthesize 'halide free' complexes were performed by reacting *trans*-[Pd(PEA)₂Cl₂] with potassium hydroxide, when the bis-chelate complex *trans*-[(PEAat)₂Pd] was formed. The preferred neutral coordination mode of the applied ligands was exhibited in the crystallization of [(BPEA)MCl₂] (M = Pd, Cu). All complexes were obtained as crystalline solids and important structural motifs were elucidated via single crystal XRD studies. In addition, the palladium complexes were investigated in solution by NMR spectroscopy. The copper complexes were analyzed towards their different structures in solution and in the solid-state by EPR spectroscopy.

Furthermore, the compounds *trans*-[Pd(MOEA)₂X₂] were successfully used as precursors for the microwave-assisted synthesis of palladium nanoparticles. It could be shown that the resulting particle shape depended upon the halide substituents. The influence of different reaction conditions on the particle size and shape was analyzed. The preliminary studies on the catalytic activity of the palladium nanoparticles in C–C cross-coupling reactions (*Heck*, *Suzuki-Miyaura*, *Sonogashira*) resulted in high turnover numbers probably due to the homogeneous dispersion of the Pd nanoparticles in porous wooden matrices. Monodisperse, spherical copper nanoparticles were prepared from copper squarate dihydrate in a hot injection reaction. The particles formed were characterized extensively and due to an exchange of the surface ligands their solubility properties could be modified.