Abstract

Within this work 18 new mononuclear and 5 dinuclear, cylometallated Palladium(II) complexes have been synthesized. The palladium(II) cations of the dimeric species are connected by two bridging chloride anions. The mononuclear complexes carry either a ligand of the type $^{-}$XPhbpy (2-XPhenyl-2,2'-bipyridine, while X = H, F, Cl, Br. OH, OMe, OTf) or a 2,6-bis or 2,4,6-trissubstituted pyridine ligand showing a C^N^N binding motive. The 2-position is equipped with a carbanionic aryl moiety, while the 6-position either contains a thiazole or a benzothiazole unit. The reaction of HC^N^CH ligands of the diphenylpyridine-type did not yield dicyclopalladated complexes. Instead this reaction lead, as well as the reaction of C^N ligands, to dinuclear, di-chlorido bridged complexes. This finding could be confirmed by an X-ray crystal structure determination of $[Pd(PhPy)Cl]_2$ (PhPy = 2-Phenylbipyridine).

All protoligands (ligand precursors) have either been prepared via *Kröhnke* pyridine synthesis or were build up in a multistep synthesis starting from 2,6-Dibromopyridine. The metalation was achieved by reacting the protoligand with potassium tetrachloropalladate(II) in a boiling mixture of water and acetonitrile.

The optical properties of all protoligands and complexes were examined via UV/Vis spectroscopy. While the protoligands only show absorption in the UV region, a broad band at around 400 nm is present in all complexes. This band can be assigned to metal-to-ligand charge-transfer (MLCT). [Pd(OHPhbpy)Cl] (6-(6-Hydroxyphenyl-2-id)-2,2'-bipyridine-chlorido-palladium(II)) falls out of the line by showing two broad absorption bands a 394 and 460 nm. The simulated spectrum of this complex by TD-DFT methods allows the assignment of those bands to again mainly metal-to-ligand charge-transfer. But an interligand charge transfer (LL'CT) from the halogenido coligand to the lowest unoccupied molecular orbital (LUMO), which is mainly localized on the thiazole moiety, plays a role as well.

The electrochemical potentials of the first reduction wave were determined by cyclic voltammetry. The protoligands as well as the complexes show differences in their potentials up to several hundreds of mV depending on the incorporation of a thiazole or a benzothiazole unit. The idea of the LUMO being localized mainly on this substituent can be backed-up by calculations on DFT-level as well as on the results in UV/Vis spectro-electro chemical measurements (SEC). Electrochemical oxidation could be only observed in very rare cases during CV-experiments. This is due to their high potentials above 0,8 V. Only in rare cases an irreversible oxidationwave with lower potentials could be observed. DFT calculations predict a metal-centered oxidation with a high participation of the chloride coligand.