

Abstract

The subject of the presented work is synthesis and characterisation of transition metal complexes of iron, iridium and nickel. EPR spectroscopy as well as spectro-electrochemical methods was applied for the investigation of electronic states in transition metal complexes some of which are labile.

The synthesis of the iron-complex $(\text{PPh}_4)[(\text{bpy})\text{Fe}(\text{CN})_3(\text{NO})]$ could be reproduced successfully. The assumption of the system being $\{\text{Fe}(\text{NO})\}^{7-}$ or $\{\text{Fe}^{\text{II}}(\text{NO}^\bullet)\}$ type was validated using a variety of combined spectroscopic (EPR, UV/vis- and IR) and spectro-electrochemical methods. The oxidation leading to a $\{\text{Fe}(\text{NO})\}^6$ system is reversible on the time scale of all applied methods and the spectroscopic data shows the features of a $\{\text{Fe}^{\text{II}}(\text{NO}^+)\}$ -system. The reduction to a $\{\text{Fe}(\text{NO})\}^8$ system is irreversible and no information could be obtained regarding the nature of the resulting product.

The reaction of the $\{\text{Ir}(\text{NO})\}^6$ -type complex $[\text{IrCl}_5(\text{NO})]^-$ with different primary amines yielding a number of stable complexes $[\text{IrCl}_5(\text{N}(\text{O})\text{N}(\text{H})\text{R})]^{2-}$ containing otherwise unstable primary aliphatic nitrosamines as ligands. The decomposition of these complexes by OH^- cleavage upon treatment with acids was already known to yield diazonium complexes. This work gives detailed insight into the behaviour of the nitrosamine complexes upon electrochemical and chemical oxidation using a combination of analytical methods. The electrochemical oxidation is reversible on the time scale of cyclic voltammetry. UV/vis-spectroscopic measurements could prove that the products of the electrochemical as well as the chemical oxidation are identical. NMR spectroscopy after chemical oxidation clearly hints towards the formation of a diazonium complex. This shows that chemical as well as electrochemical oxidation yields the same diazonium complex that was observed after acid treatment, but with different compounds being formed in the process. Upon oxidative activation, the formation of the diazonium complex occurs after cleavage of an $\bullet\text{OH}$ radical.

Five new ligands based on 2,5-bis(1-phenyliminoethyl)pyrazine (bpip) were designed, synthesised and thoroughly characterised for the synthesis of $[(\mu\text{-N}^{\wedge}\text{N})\{\text{Ni}(\text{Mes})\text{Br}\}_2]$ type binuclear Ni(II) complexes. However, the isolation of those complexes was not possible due to the electron deficient character of the ligands. It could be shown that these complexes can be investigated without isolation using *in situ* synthesis or titration methods. Unlike most known complexes of methyl-substituted derivatives of the bpip ligands, these complexes show higher wavelength absorptions and higher reduction potentials. This should slow down

the rate of cleavage of the bromido ligand compared to the known complexes of that type, which makes those compounds promising being potential catalysts for C–C cross-coupling reactions.

Two new penta-coordinated Ni(II) complexes [(terpy)Ni(CF₃)₂] and [(*t*Bu₃terpy)Ni(CF₃)₂] were synthesised and characterised. Those complexes can be electrochemically oxidised to yield a [(R₃terpy)Ni(CF₃)₂]^{•+} type Ni(III) complex that was investigated using EPR spectroscopy. The Ni(III) complex decomposed under formation of a cationic [(R₃terpy)Ni(CF₃)]⁺ complex and a •CF₃ radical. The formation of this radical could be proven using spectro-electrochemical EPR spectroscopy in the presence of a PBN spin-trap.