

Electrochemical redox behavior of Pt(II)-N-heterocyclic carbene complexes: An in-situ IR spectroscopy study

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Transition metal complexes with N-heterocyclic carbene (NHC) ligands show unique steric and electronic properties and are applied in fields such as (electro)catalysis and materials science.^[1,2] In this work, we characterize a PtII(NHC)₂Cl₂ complex in which the NHC ligands form a square planar coordination environment. The redox behavior of PtII(NHC)₂Cl₂ on polycrystalline Pt electrodes was monitored by in-situ electrochemical infrared reflection absorption spectroscopy (EC-IRRAS) combined with density functional theory (DFT). The study was complemented by cyclic voltammetry (CV) and nuclear magnetic resonance (NMR) spectroscopy measurements. The reduction of the complex occurs in two steps at -2.30 and -2.43 V_{fc} and is reversible. We observe reduced species showing a clear redshift (115 cm⁻¹) in the IR spectrum and an increase in intensity of the nitrile band. By comparing experimental spectra with modelling, we identify the formation of [Pt(NHC)₂Cl_x]^{z-} complexes with mesomeric charge delocalization on the two NHC ligands. This leads to an elongation of the CN bond and, as a result, induces the observed redshift of the nitrile band and the increase in the dynamic dipole. Our result demonstrates the important role which the NHC ligands play for the electrocatalytic behavior.

[1] D. Broere *et al.*, Chem. Soc. Rev., 2015, **44**, 6886. DOI: 10.1039/C5CS00161G

[2] I. Mikhailov *et al.*, Catalysts, 2023, **13**, 1291. DOI: 10.3390/catal13091291