

Redox Chemistry of Ruthenium Metallocenes with Polycyclic Aromatic or Cyclophane Ligands

Bernd Speiser

Universität Tübingen, Institut für Organische Chemie
Auf der Morgenstelle 18
D - 72076 Tübingen
Germany

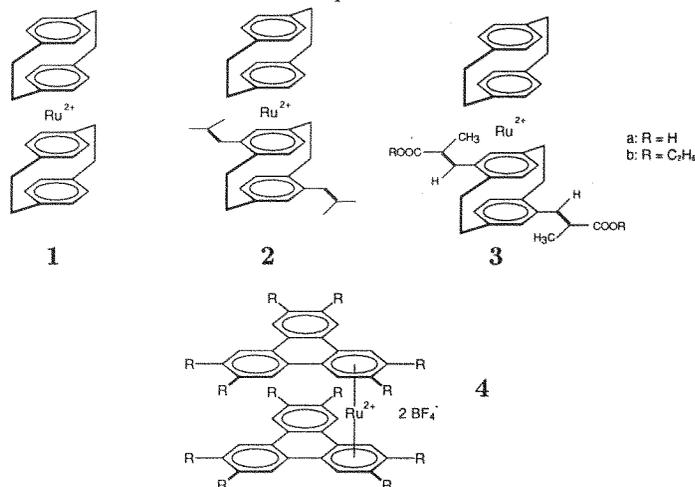
Stefan Dümmling

Universität Tübingen, Institut für Organische Chemie
Auf der Morgenstelle 18
D - 72076 Tübingen
Germany

Ioannis Zagos

Universität Tübingen, Institut für Organische Chemie
Auf der Morgenstelle 18
D - 72076 Tübingen
Germany

Metallocene type complexes of ruthenium (Ru^{2+} as central atom; in all cases BF_4^- as counter ion



have attracted interest recently [1,2] as possible building blocks for polymetallocene stacks with unusual electronic and conducting properties [3]. As such, the redox properties of these complexes belong to the most important basic facts for the assessment of their use. Furthermore, it has been suggested that electrochemical redox processes may be helpful in the synthesis of the desired materials [1].

Here, we report on the *reduction and oxidation* behavior of complexes 1 – 4. All compounds can be reduced, while 2 and 3 show an additional irreversible oxidation.

The reduction of 1 – 4 is a two-electron process similar to bis(hexamethylbenzene)ruthenium(II) [4,5]. It was investigated in detail in dichloromethane, propylene carbonate, and *o*-dichlorobenzene as solvents (0.1 M NBu_4PF_6 as supporting electrolyte; glassy carbon disk electrodes) with cyclic voltammetry (CV), chronoampero- and coulometry including simulation of the CV results (Digisim). The difference of formal potentials and the heterogeneous electron transfer rate constants for the two redox steps depends on the ligand structure and on the solvent properties. These systems show highly compressed 1 – 3 or even inverted (4) potentials. Simulations with an EE reaction model proved successful in reproducing the experimental results at various scan rates and concentrations.

No oxidation is observed for 1 and 4. Voltammograms of complexes 2 and 3, however, exhibit an oxidation peak. Depending on solvent, electrode material, and type of complex, the irreversible follow-up reactions induced by the corresponding electron transfer lead to filming and modification of the electrode with redox-active material. These processes were followed by cyclic voltammetry and experiments at an electrochemical quartz crystal microbalance (electrogravimetry). It has recently been shown [6] that vinyl-substituted cyclophanes can be polymerized through electrochemical oxidation of the $-CH=CH_2$ moiety. In analogy, we assume that the complexes investigated here form insoluble oligo- or polymers containing redox active Ru centers upon oxidation. During redox cycling the films dissolve, and the dissolution process was also studied by electrogravimetric experiments.

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