Chemical and Photochemical Water Oxidation by [RuCl (NC^{NHC}O)(DMSO)(py)]-Type Complexes

Suammary:

Incorporation of negatively charged moieties into complexes is a promising strategy to develop water oxidation catalysts with high stability and low over-potentials. In this regard, we reported here the synthesis of a novel pincer-type ligand precursor, 1-(pyridin-2-ylmethyl)-3-methylcarboxylate-imidazolium and then the effects of substitutions in the backbone of imidazolylidene and axial ligands on the reactivity and stability of water-oxidation catalysts were investigated. Three pincer-type asymmetric imidazolium salts **NC^{NHC}O**, **NC$^{NHC\text{-}4Br}$O**, and **NC$^{NHC\text{-}B}$O** (NHC: N-heterocyclic carbene), of which the donating ability of the corresponding imidazolylidene decreases in the same sequence, were prepared. Their application in metalation afforded the corresponding Ru complexes **1 a**, **1 b**, **2**, and **3**. It was found that the complexes incorporating the stronger donor displayed lower potential for each redox couple and longer lifetimes, but relatively low reaction rates. Under acidic conditions, water oxidation driven by cerium ammonium nitrate resulted in turnover numbers (TONs) of 2322, 1728, 1928, and 2208 for **1 a**, **1 b**, **2**, and **3**, respectively. Complex **2** exhibited a good match of reactivity and stability with a TON of 136 in a typical three-component photocatalysis. Importantly, NHCs could be another powerful tool for tuning the reactivity and stability of water-oxidation catalysts, in addition to substituted pyridines. Rational orchestration of modified NHCs and pyridines could eventually result in water-oxidation catalysts exhibiting appreciable effectiveness and considerable robustness.

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