Substantial Improvement of Pyridine-Carbene Iridium Water Oxidation Catalysts by a Simple Methyl-to-Octyl Substitution

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Molecular water oxidation catalysts are receiving much attention since their performance can potentially be tailored and optimized by an appropriate selection of the ancillary ligands. [1-2] Herein we show that the substitution of a methyl to an octyl group in the ancillary triazolylidene ligand—an apparently simple variation—induces a more than 10-fold increase of activity of the corresponding iridium complex in water oxidation catalysis when using cerium(IV) as sacrificial oxidant. Detailed NMR studies suggest that various different molecular species form, all bearing the intact triazolylidene ligand. The octyl substituent is essential for inducing the association of the iridium species thus generating extraordinarily active multimetallic catalytic sites. Their accessibility and steady state concentration is critically dependent on the type of sacrificial oxidant and specifically on the CAN vs catalyst ratio.

In conclusion, while the incorporation of lipophilic elements into a catalyst for water oxidation appears highly counterintuitive, the introduction of long alkyl chains may become an essential feature when designing molecular water oxidation catalysts with exceptionally high activity, also when considering metal complexes other than those based on iridium.

References

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