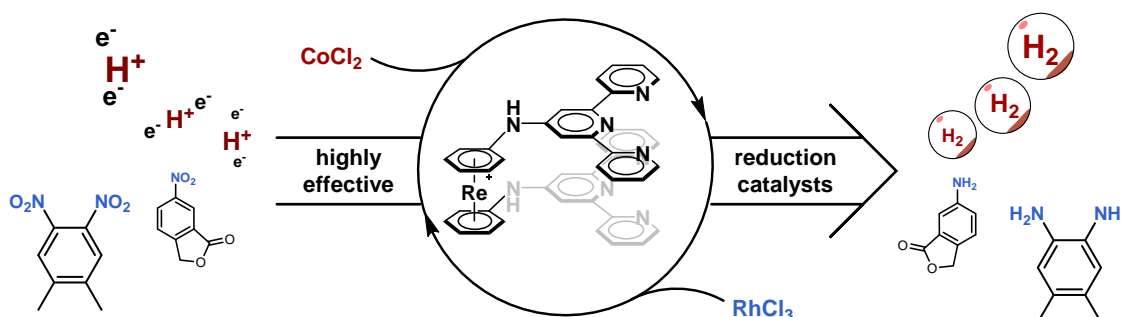


$[\text{Re}(\eta^6\text{-arene})_2]^+$ SCAFFOLDS ARE ATTRACTIVE HOSTS FOR METAL-TERPYRIDINE CATALYSTS

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We have been investigating the rich chemistry of $[\text{Re}(\eta^6\text{-arene})_2]^+$ over the recent years. These sandwich complexes are a highly stable and water-soluble alternative to ferrocene for fundamental and applied research.^[1-2] Terpyridine (terpy) complexes are well-established catalysts, building blocks of supramolecular chemistry and sensors in life sciences.^[3-4] We combined $[\text{Re}(\eta^6\text{-arene})_2]^+$ with terpy chelators to investigate how this conjugation would affect the activities of the conjugated metal-terpy complexes. Furthermore, we ask if metal-to-metal cooperativity can be induced by attaching two terpy to $[\text{Re}(\eta^6\text{-aniline})_2]^+$ followed by complexation with transition metals.



We present the mono- and bis-substituted $[\text{Re}(\eta^6\text{-C}_6\text{H}_5\text{-R})_2]^+$ (R=H or -NH-4'-terpy) conjugates. Complexation with Fe(II), Co(II), Ni(II), gave $[\text{M}[\text{Re}(\eta^6\text{-C}_6\text{H}_5\text{-R})_2]_2]^{4+}$ and with Cu(II), Rh(III) and Pt(II) the $[\text{M}[\text{Re}(\eta^6\text{-C}_6\text{H}_5\text{-R})_2]\text{Cl}_n]^{m+}$ compounds.

To assess the influence of the $[\text{Re}(\eta^6\text{-C}_6\text{H}_5\text{-R})_2]^+$ sandwiches to the native catalysts, we compared $[\text{Re}(\eta^6\text{-C}_6\text{H}_6)(\eta^6\text{-C}_6\text{H}_5\text{-NH-terpyRhCl}_3)]^+$ against $[\text{Rh}(\text{terpy})\text{Cl}_3]$ in catalytic nitroarene to aniline reduction in aqueous media and found both catalysts to perform equally well in turnover numbers and substrate scope. We observed though no cooperativity between the two $\{\text{Rh}(\text{III})\text{terpyCl}_3\}$ entities in $[\text{Re}(\eta^6\text{-C}_6\text{H}_5\text{-NH-terpyRhCl}_3)_2]^+$. Preliminary results demonstrate that $[\text{Co}([\text{Re}(\eta^6\text{-C}_6\text{H}_5\text{-R})_2]_2)]^{4+}$ are suitable water reducing catalysts in both electro- and photocatalytic systems.

We demonstrate the potential of the $[\text{Re}(\eta^6\text{-aniline})_2]^+$ scaffold as a versatile tool for the attachment of metal terpyridine complexes without compromising their activities. Along our approach, other chelators can equally well be introduced. Whether these systems facilitate metal-to-metal cooperativity is subject of further investigations.

[1] D. Hernández-Valdés, R. Fernández-Terán, B. Probst, B. Spingler, R. Alberto, *Helv. Chim. Acta* **2020**, 103, e2000147.

[2] D. Hernández-Valdés, F. Avignon, P. Müller, G. Meola, B. Probst, T. Fox, B. Spingler, R. Alberto, *Dalton Trans.* **2020**, 49, 5250-5256.

[3] C. Wei, Y. He, X. Shi, Z. Song, *Coord. Chem. Rev.* **2019**, 385, 1-19.

[4] J. Karges, K. Xiong, O. Blacque, H. Chao, G. Gasser, *Inorg. Chim. Acta* **2021**, 516, 120137.