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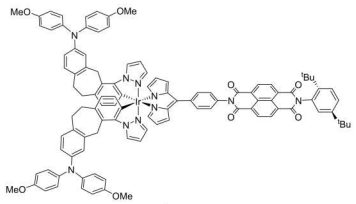
Coordination Chemical Scaffold

for Dual Proton Coupled Photoelectron Transfer

Mareike Hüttenschmidt, Alexander Villinger and Wolfram W. Seidel*

Introduction



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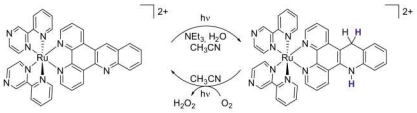
In photochemistry, the investigation of charge and electron transfer mechanisms are of crucial importance to understand and optimize the possible applications of photo energy. One key step in biological and artificial systems is the charge separation (CS) to generate states that exhibit a long life time. A well-known structure for CS is the Y-shaped assembly with bridged electron-donor and electron-acceptor ligands. The bridging moiety can either be a pure organic spacer or include an active chromophore. Lambert et al. reported a complex **1** containing an Ir(III)-centre which shows a CS-state with a life time of about 0.6 µs.[1] Another interesting concept is the NAD^+/NADH redox system which shows the highest reducing ability of any biological systems. Tanaka et al. showed that their complex **2** with a Ru(II)-centre can be reduced under visible light irradiation in the presence of triethylamine in an acetonitrile/water mixture. The energy transfer from the excited NADH-form **3** to triplet oxygen allows photoreduction of the generated singlet oxygen to form H_2O_2.[2]



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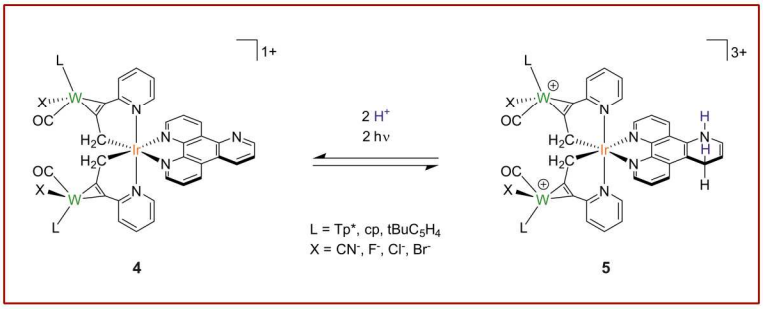
This work: Synthesis of a new Y-shaped complex for PCET

The essential concept of this project is the assembly of classical photo-active centres like an Ir(III) or Ru(II) polypyridine complex unit with two redox-active, potentially electron donating metalloligands and Brønstedt-basic two-electron acceptor as NAD/NADH model in an Y-shaped arrangement (**4**). Within this frame, novel redox-active N,C-κ^2-donating ligands including an alkyne complex moiety, which bears terminal donor functionalities, are the central invention. The redox activity of the electron donating ligands is based on the redox activity of the side-on alkyne coordinated metal.



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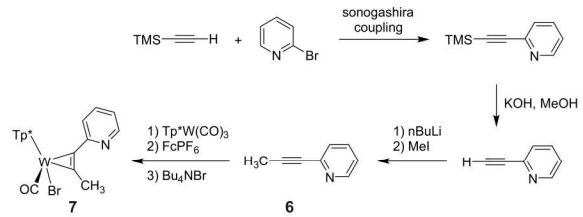
The inherent problem of unproductive charge recombination of a comparatively compact CS triad is addressed by chemical state trapping by protons and subsequent radical pair formation. A 2,3-5',6'-fused pyridylphenanthroline derivative was chosen as an appropriate NAD/NADH model ligand. The complex **4** should be able to undergo a dual proton coupled photo-electron transfer (PCET) to form the comparatively stable state **5**. The needed double pulse excitation in appropriate time-resolved transient absorbtion experiments will be performed in collaboration with the Lochbrunner group.

Synthetic Approach

Synthesis of the electron donating ligand



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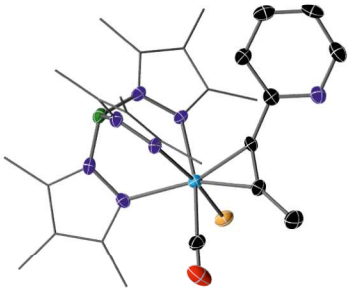
The synthesis and characterisation of redox-active compounds containing α-donor-substituted alkynes is one of the main research topics of the Seidel group.[3] Therefore, the reaction of free or protected alkynes with suitable precursors to the final complexes are a well known route to obtain these moities. To generate the desired complex (**7**) a sonogashira reaction of TMS-acetylene and 2-bromopyridine, followed by removal of the TMS-protecting group and methylation in α-position leads to the required alkyne (**6**).[4] A one-electron oxidation of $Tp^*W(CO)_3$ and subsequent reaction with alkyne **6** gives a cationic dicarbonyl compound, which is in turn reacted with Bu_4NBr as a bromide source to give the neutral, air-stable complex ligand **7** in 40 % yield. The CV establish the desired low oxidation potential at about -27 mV vs Fc/Fc^+.



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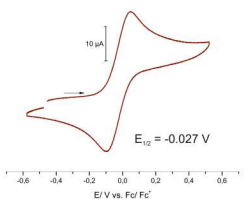
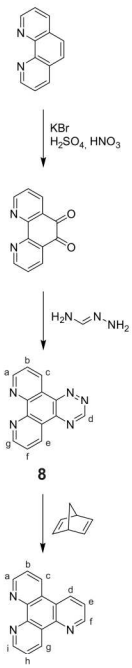


Fig. 1: Cyclic voltammogram of **7** in CH_2Cl_2 (0.10 M n-Bu_4NPF_6, 100 mV/ s, vs Fc/Fc^+).

Synthesis of the NAD/NADH model ligand



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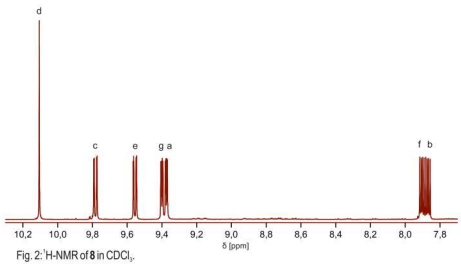

Fig. 2: ^{1}H-NMR of **8** in $CDCl_3$.

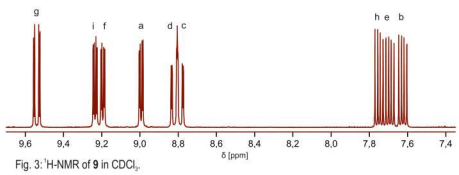

Fig. 3: ^{1}H-NMR of **9** in $CDCl_3$.

The synthesis of the 2,3-5',6'-fused pyridylphenanthroline derivative starts with an oxidation of the 1,10-phenanthroline using H_2SO_4, HNO_3 and KBr to form phenanthroline-5,6-dione in a good yield.[5] Following the procedure of Sauer et al., we have optimized the synthesis of **8** and **9** to obtain yields of 60- 70%. The condensation of phenanthroline-5,6-dione with the in situ generated formamidrazone leads to the 1,2,4-Triazino[5,6-f][1,10]-phenanthroline (**8**). Finally, a cycloaddition of norbornadien and the triazine moiety of **8** followed by a cycloelimination of dinitrogen and cyclopentadiene generates the desired product (**9**).[6]

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INSTITUT FÜR CHEMIE| **Universität Rostock,** Albert-Einstein-Straße 3a | 18059 Rostock | Germany