

Resolving the CO₂ addition step: Transient IR Spectroscopy of PNN- and AsNN- Rhenium(I) tricarbonyl complexes

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Introduction

We used electrochemical, spectroelectrochemical and time resolved spectroscopy to study of the reactivity of Re tricarbonyl complexes with 8-(diphenylphosphanyl)quinoline and 8-(diphenylarsanyl)quinoline ligands with CO₂ in comparison with *fac*-Re(bpy)(CO)₃Cl (bpy=2,2'-bipyridine or 4,4'-dimethyl-2,2'-bipyridine). We found differences in the reactivity of the singly reduced complexes towards the exchange of the axial ligand for CO₂ (or solvent).

Results

Visible-pump-IR-probe experiments on the 20ps–1μs timescale of RePNN and ReAsNN show a high quantum yield for photoreduction with different electron donors.

Additional electrochemical studies of RePNN in presence of CO₂ suggest that the singly reduced RePNN complex reacts with CO₂ on timescales shorter than 1-2 s.

This finding was the motivation for the time resolved IR spectroscopic studies of RePNN in presence of CO₂ and a sacrificial electron donor on timescales from picoseconds up to 1s which supports the proposed reaction pathway shown on the right.

Spectroelectrochemistry

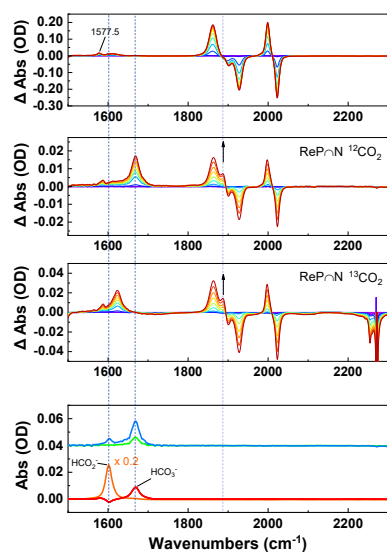
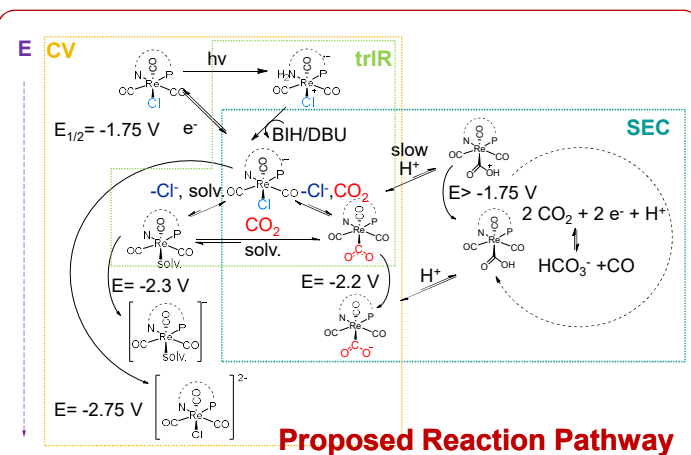
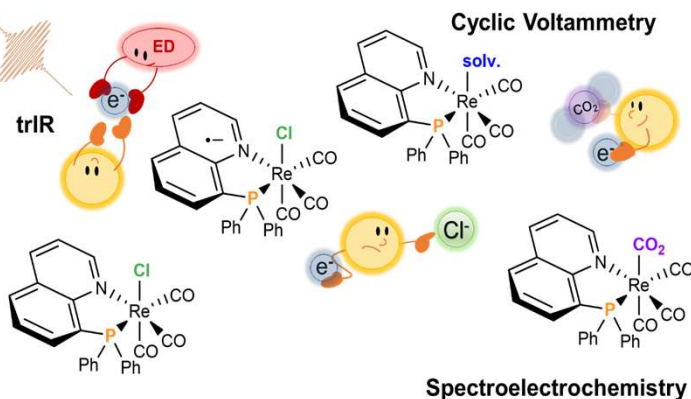
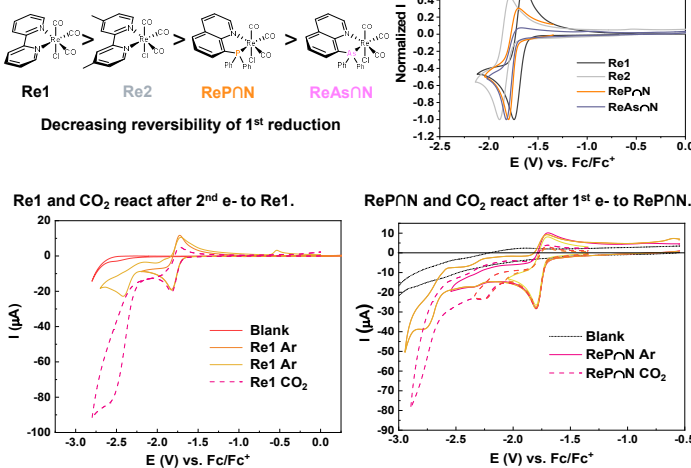


Figure SEC of first reduction of ReP with Ar or CO₂ in DMSO/ 0.3 M TBAPF₆ solution (black line: ¹²CO₂ alone at -2.2 V)



Cyclic Voltammetry



Figures CVs of Re complexes in DMF/0.1 M TBAPF₆ with Ar (full lines) or CO₂ (dashed lines) on a GC-WE. Ferrocene as internal standard. The scanrate was 50mV/s.

tr-IR Studies

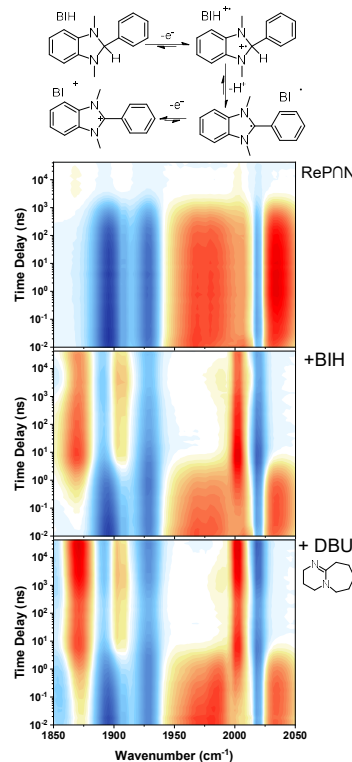


Figure ps-μs trIR data of RePNN in DMSO with BIH as electron donor and DBU as a non-nucleophilic base.

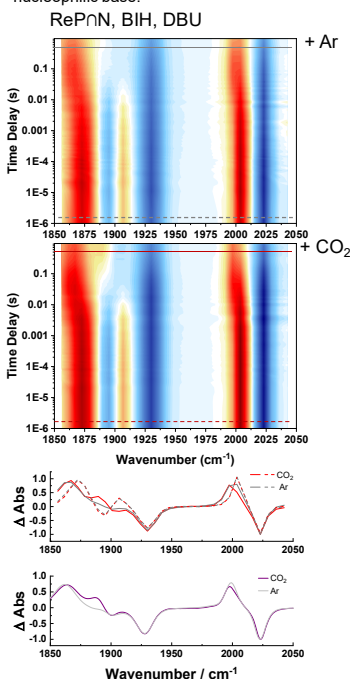


Figure μs-s trIR data of RePNN in DMSO with BIH and DBU in presence of either Ar or CO₂. Top: Contour plots. Middle: Transient cuts at early and late delays. Bottom: SEC transients of RePNN upon single electron reduction in presence of either CO₂ or Ar.

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References

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