

# REDUCTIVE CHEMISTRY OF (ALKYL)FORMAZAN(CO)<sub>3</sub>Re(I) COMPLEXES: AN (SPECTRO)ELECTROCHEMICAL STUDY

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The redox-active formazanate ligand is a versatile scaffold. The richness of its coordination chemistry and photophysical/electrochemical properties emerge from having a flexible, conjugated nitrogen-rich backbone with low-lying  $\pi$ -orbitals. [1] Several reports have described its capability to serve as an electron reservoir when coordinated to main group and  $d$ -block elements, a trait attractive for redox transformations. [2] Recently, we reported the synthesis and characterization of rhenium complexes with neutral, protonated formazans, in which these ligands coordinate in the *open* form to result in a five-membered chelate ring. [3] We envisioned that the pendant NH group in these complexes could be further functionalized or exploited as a proton-responsive group. Herein, we describe a comparative (spectro)electrochemical study between the neutral formazan and alkylformazan Re(I) complexes of the type *fac*-Re(CO)<sub>3</sub>(N<sup>3</sup>,N<sup>1</sup>) (N<sup>3</sup>,N<sup>1</sup> = PhN<sup>4</sup>(R)N<sup>3</sup>=C(H)-N<sup>2</sup>=N<sup>1</sup>Ph; R = H, Me). Our outcomes indicate that methylation of the proton responsive group stabilizes the redox states derived from the reduction of formazan-like Re(I) species (Figure 1).

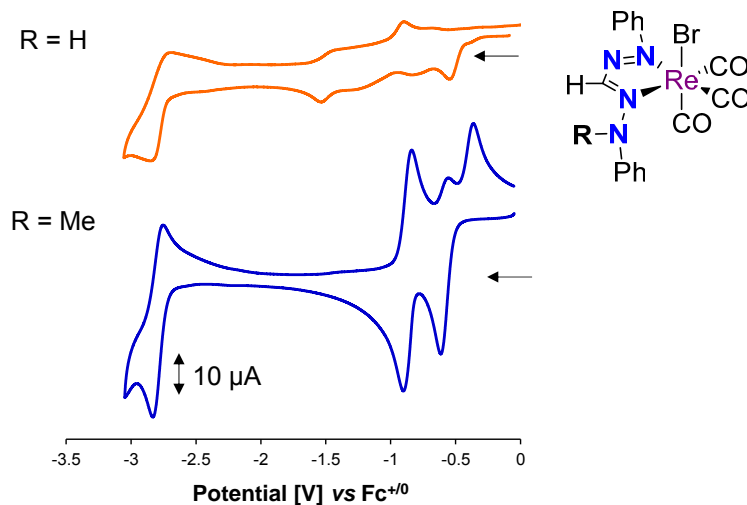


Figure 1. Comparative electrochemical behavior in (alkyl)formazan Re(I) species.

[1] Gilroy, J. B.; Otten, E *Chem. Soc. Rev.* **2020**, *49*, 85–113.

[2] (a) Gilroy, J. B.; Ferguson, M. J.; McDonald, R.; Patrick, B. O.; Hicks, R. G. *ChemComm.* **2007**, 412, 126–128. (b) Chang, M. C.; Roewen, P.; Travieso-Puente, R.; Lutz, M.; Otten, E. *Inorg. Chem.* **2015**, *54* (1), 379–388.

[3] Capulín Flores, L.; Paul, L. A.; Siewert, I.; Havenith, R.; Zúñiga-Villarreal, N.; Otten, E. *Inorg. Chem.* **2022**, *61*, 13532–13542.