1. The following Fe complex is a molecular electrocatalyst for hydrogen evolution. Propose a catalytic cycle for this Fe-catalyzed hydrogen evolution. Specify the oxidation states of the Fe complexes. The initial iron complex before reduction is Fe(II). You don't need to draw the macrocyclic ligand; abbreviate it as "N4", e.g., [FeII(N4)(py)] would be sufficient for the complex in the graph.

$$C_{6}F_{5}$$

$$C_{6}F_{5}$$

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$$C_{6}F_{5}$$

$$C_{6}F_{5}$$

One possibility

$$[Fe^{II}(N_4)(py)] + e = [Fe^{I}(N_4)(py)]^{-}$$

$$[Fe^{I}(N_4)(py)]^{-} + H^{+} = [H-Fe^{III}(N_4)(py)]$$

$$[H-Fe^{III}(N_4)(py)] + H^{+} = [Fe^{III}(N_4)(py)]^{+} + H_2$$

$$[Fe^{III}(N_4)(py)]^{+} + e = [Fe^{II}(N_4)(py)]$$

A second possibility:

$$\begin{split} &[Fe^{II}(N_4)(py)] + e = [Fe^{I}(N_4)(py)]^- \\ &[Fe^{I}(N_4)(py)] + e = [Fe^{0}(N_4)(py)]^{2-} \\ &[Fe^{0}(N_4)(py)]^{2-} + H^+ = [H-Fe^{II}(N_4)(py)]^- \\ &[H-Fe^{II}(N_4)(py)]^- + H^+ = [Fe^{II}(N_4)(py)] + H_2 \end{split}$$

1. The following Fe complex is a molecular electrocatalyst for hydrogen evolution. Propose a **bimetallic** catalytic cycle for this Fe-catalyzed hydrogen evolution. Specify the oxidation states of the Fe complexes. The initial iron complex before reduction is Fe(II). You don't need to draw the macrocyclic ligand; abbreviate it as "N4", e.g., [FeII(N4)(py)] would be sufficient for the complex in the graph.

$$C_6F_5$$
 N
 O
 F
 F
 C_6F_5
 C_6F_5

One possibility

$$\begin{split} &[Fe^{II}(N_4)(py)] + e = [Fe^{I}(N_4)(py)]^- \\ &[Fe^{I}(N_4)(py)]^- + H^+ = [H-Fe^{III}(N_4)(py)] \\ &[H-Fe^{III}(N_4)(py)] + [H-Fe^{III}(N_4)(py)] = H_2 + [Fe^{II}(N_4)(py)] \end{split}$$

A second possibility:

$$[Fe^{II}(N_4)(py)] + e = [Fe^{I}(N_4)(py)]^{-}$$

$$[Fe^{I}(N_4)(py)]^{-} + e = [Fe^{0}(N_4)(py)]^{2-}$$

$$[Fe^{0}(N_4)(py)]^{2-} + H^{+} = [H-Fe^{II}(N_4)(py)]^{-}$$

$$[H-Fe^{II}(N_4)(py)]^{-} + [H-Fe^{II}(N_4)(py)]^{-} = H_2 + 2 [Fe^{I}(N_4)(py)]^{-}$$