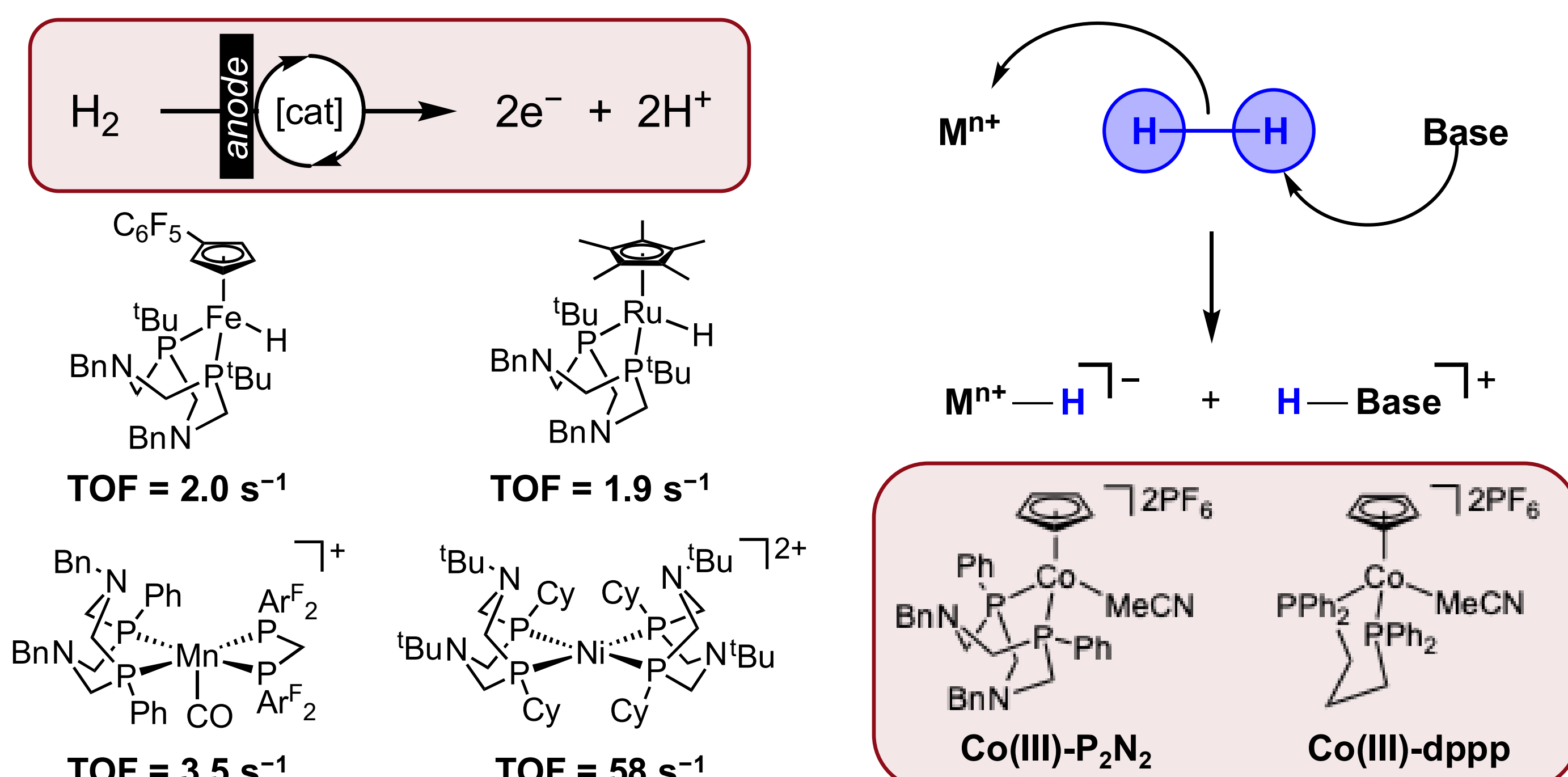


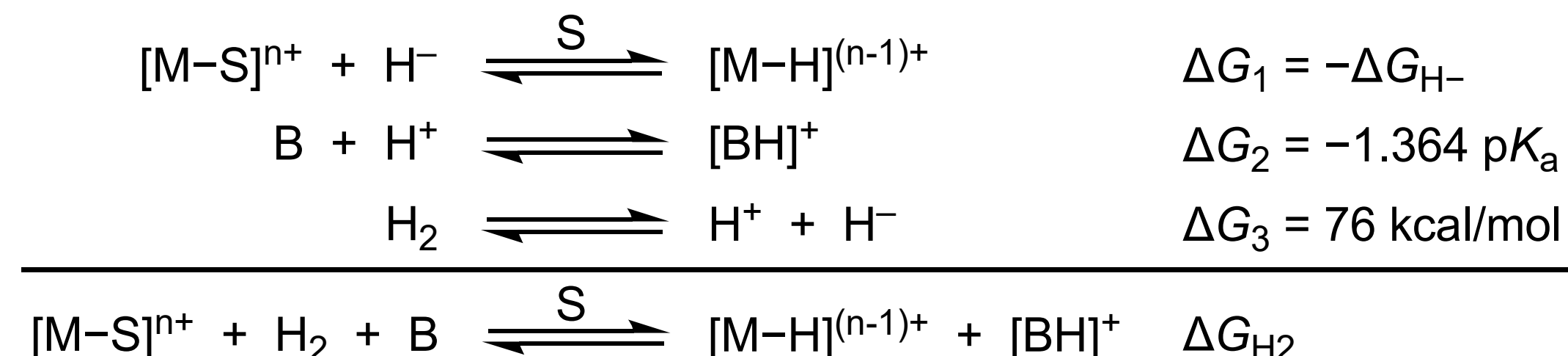
Introduction

The shift from fossil fuels to sustainable electricity sources is essential for mitigating CO₂ emissions and addressing global energy challenges. The storage of renewable energy in chemical fuels is an attractive prospective, and fuel cells can be used to harvest useable electricity via electrochemical fuel oxidation. Here, hydrogen is appealing due to its high gravimetric energy density and formation of water as the sole oxidation product. Only a few homogeneous transition metal catalysts have been reported for electrochemical H₂ oxidation. In these examples, hydrogen oxidation proceeds heterolytically, where H₂ is cleaved into a proton that is transferred to an exogenous base and hydride that is delivered to the catalyst, forming a metal-hydride complex. In this work, we show that a cobalt-phosphine complex featuring a pendent-basic ligand reacts with H₂ in a heterolytic fashion under ambient pressure, with reactivity trending as a function of base strength. The analogous complex without pendent-basic sites showed negligible activity for H₂ splitting, indicating the key role of ligand design for reactivity.



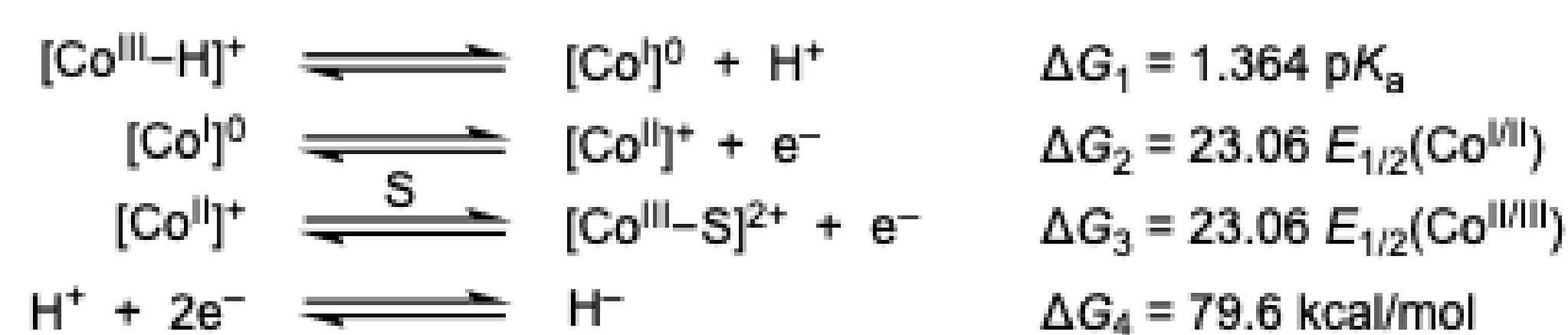
Thermodynamic Considerations

The thermodynamic favorability of heterolytic H₂ splitting depends on the hydricity of the transition metal-hydride and strength of the exogenous base:



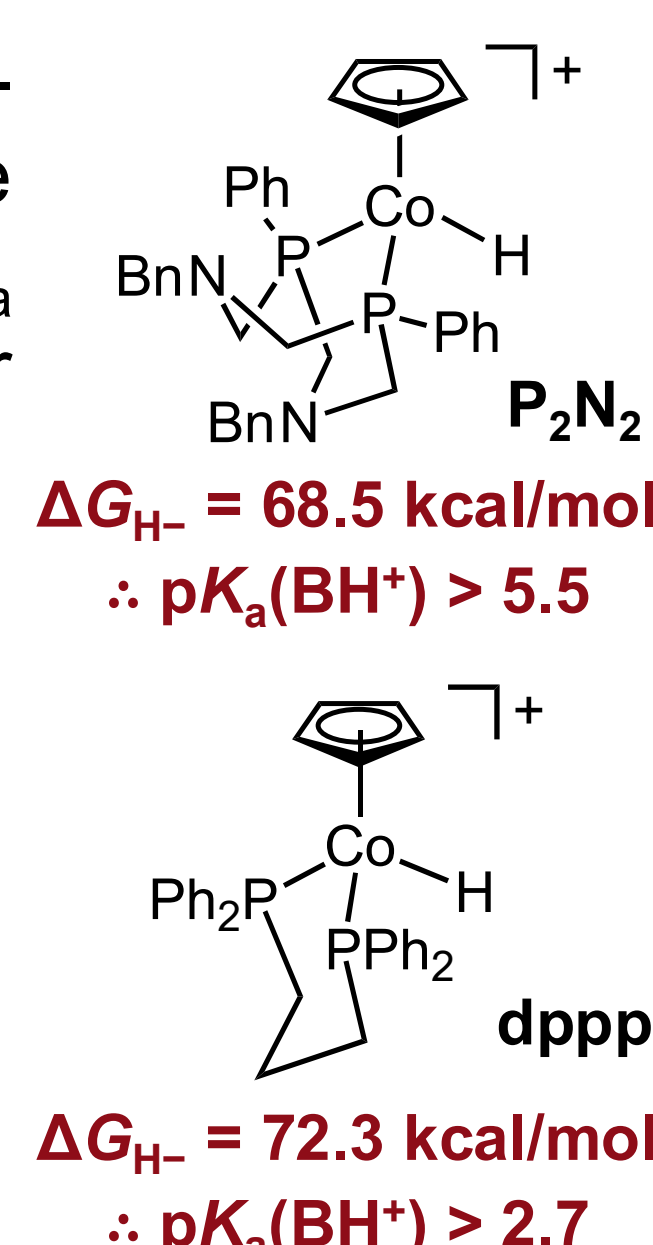
$$\Delta G_{\text{H}_2} = 76 - \Delta G_{\text{H}^-} - 1.364 \text{p}K_{\text{a}}(\text{BH}^+) \quad (\text{in MeCN})$$

Our group is interested in the oxidative reactivity of Co(III)-phosphine complexes. The thermodynamic hydricity of the Co(III)-hydrides were determined using the potential-pK_a method, from which the minimum base strength required for favorable H₂ splitting is calculated.



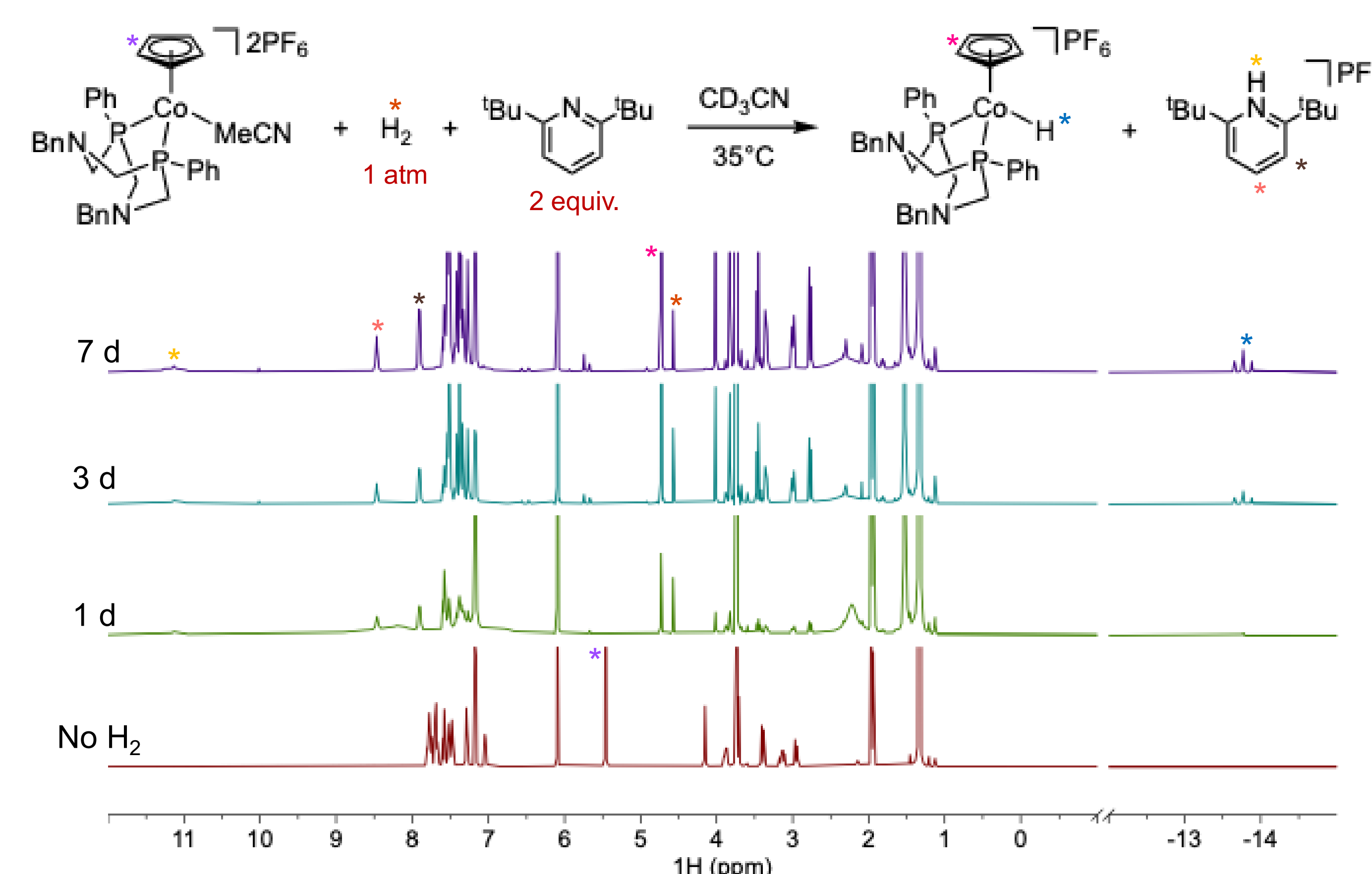
$$[\text{Co}^{\text{III}}-\text{H}]^+ \xrightarrow{\text{S}} [\text{Co}^{\text{III}}-\text{S}]^{2+} + \text{H}^- \quad \Delta G_{\text{H}^-}$$

$$\Delta G_{\text{H}^-} = 79.6 + 1.364 \text{p}K_{\text{a}} + 23.06 E_{1/2} + 23.06 E_{1/2}$$

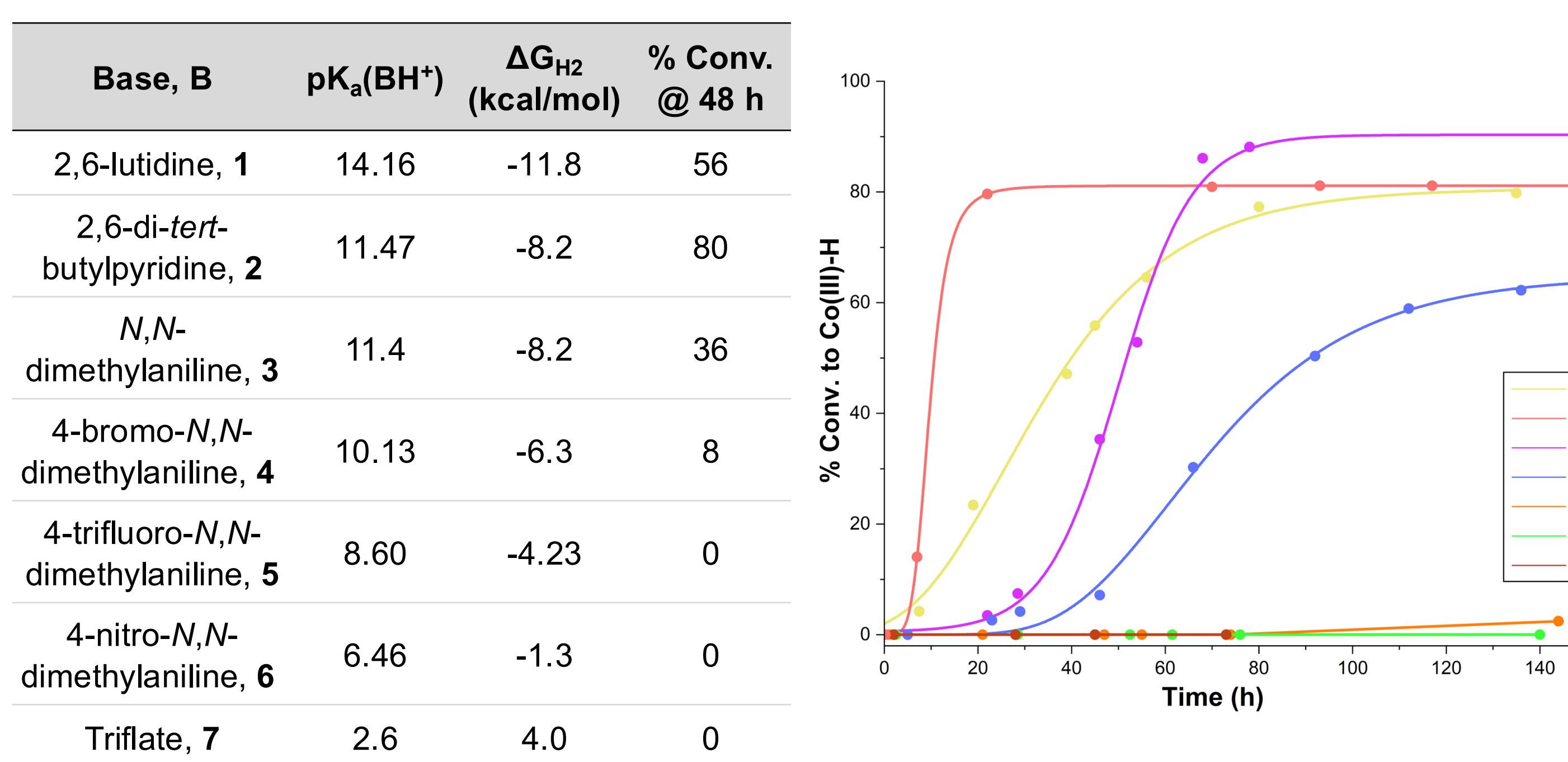
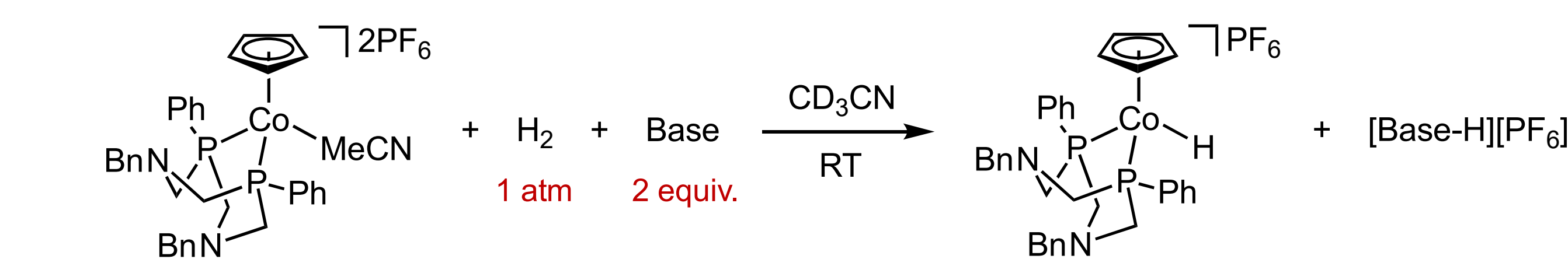


H₂ Splitting as a Function of Base

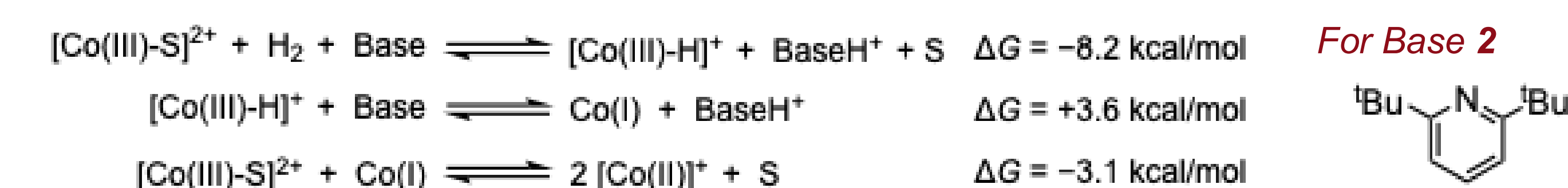
Hydrogen splitting with the Co(III)-P₂N₂ complex was studied under stoichiometric conditions under 1 atm H₂ at 35°C in the presence of various bases. Reaction progress was monitored by following the formation of the Co(III)-H complex by ¹H NMR spectroscopy.



We find that stronger bases promote faster formation of the Co(III)-H complex. Unexpectedly, we also observe an initial induction period for Co(III)-H formation, which is attributed to rapid proton and electron transfer equilibria: deprotonation of the Co(III)-H and comproportionation of Co(I) and Co(III).



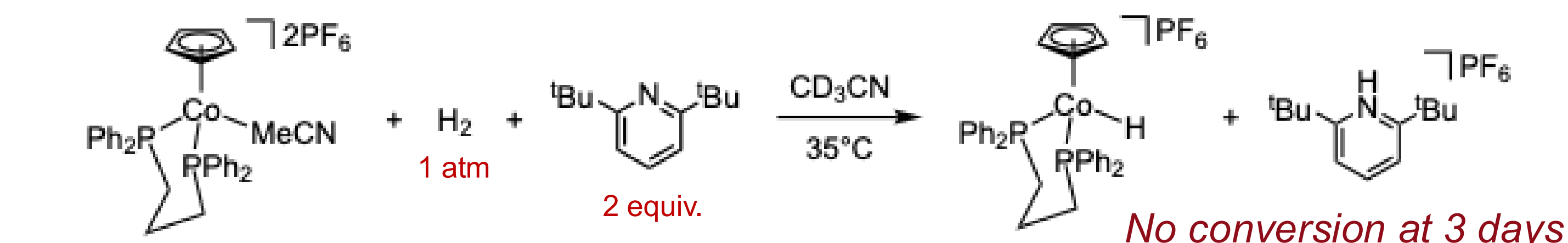
Proposed deprotonation and comproportionation equilibria after H₂ splitting:



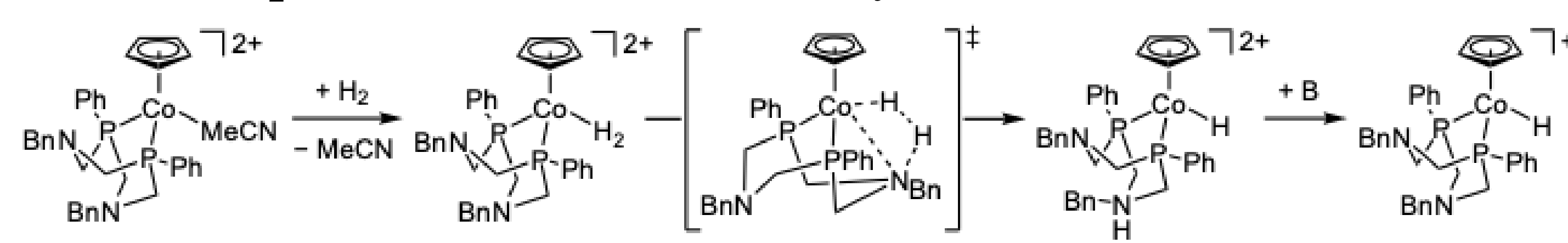
To test whether stronger bases could facilitate more rapid H₂ activation, several organic bases with pK_a > 18 were evaluated. However, in all cases, the Co(III)-P₂N₂ complex underwent decomposition to unidentified species in the presence of stronger bases.

Role of Pendent Amine in H₂ Oxidation

Studies on the analogous Co(III)-dppp complex shows negligible H₂ splitting activity, highlighting the crucial role of the pendent amine ligands in Co(III)-P₂N₂. The installation of these amine groups provides an internal proton-acceptor site that can facilitate intramolecular proton transfer for H₂ activation.



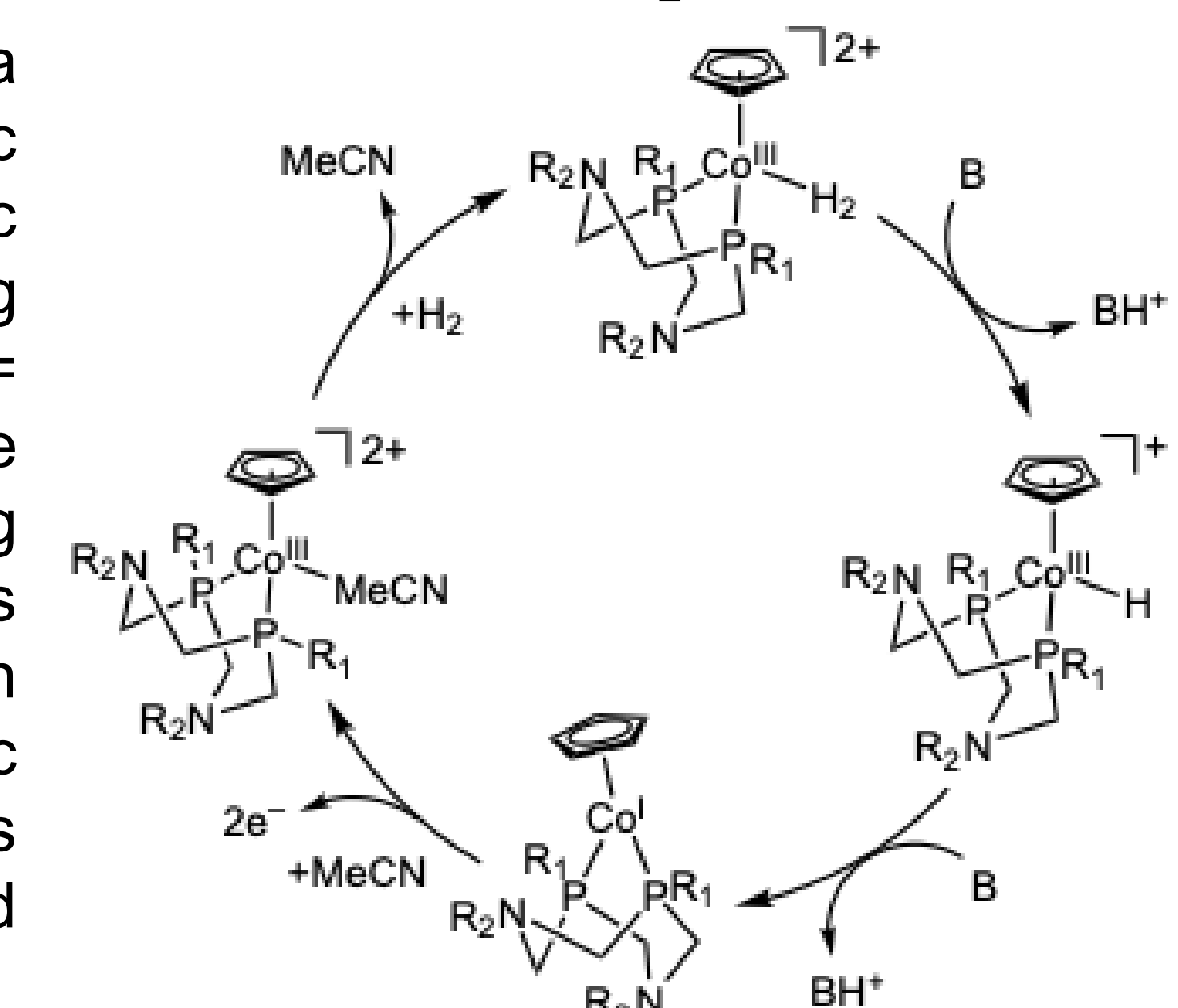
The proposed mechanism involves initial dissociation of the MeCN ligand. Following coordination of H₂ to the cobalt center, the pendent amine group assists in H₂ activation to form the cobalt-hydride bond.



Conclusions and Future Work

The Co(III)-P₂N₂ complex with a pendent-basic ligand efficiently activates H₂ via heterolytic cleavage, with hydride formation strongly influenced by the base strength. The pendent amine groups are essential, acting as intramolecular proton relays to enable facile reactivity with H₂.

Heterolytic H₂ splitting represents a key chemical step for electrocatalytic H₂ oxidation. To establish a catalytic cycle, deprotonation of the resulting Co(III)-hydride is required (pK_a = 23.1 for Co(III)-P₂N₂). However, we have found that sufficiently strong bases are not compatible with this system. Future studies will focus on tuning the steric and electronic properties of the Cp and P₂N₂ ligands to enhance complex stability and increase Co(III)-hydride acidity.



References

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