

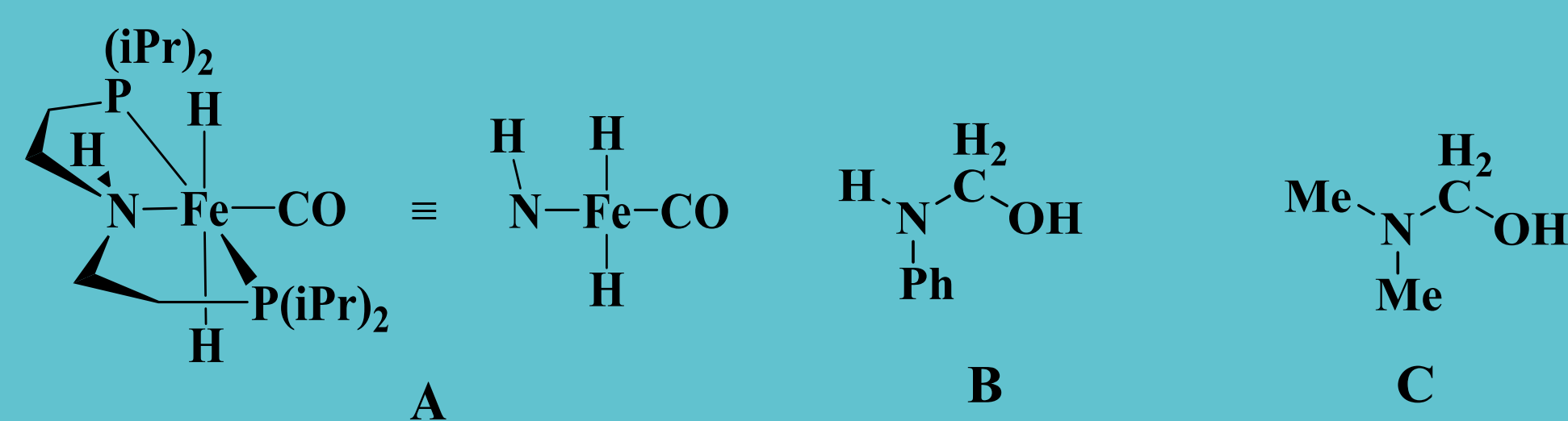
Earth-abundant metal catalyst for amide hydrogenation to methanol.

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Introduction

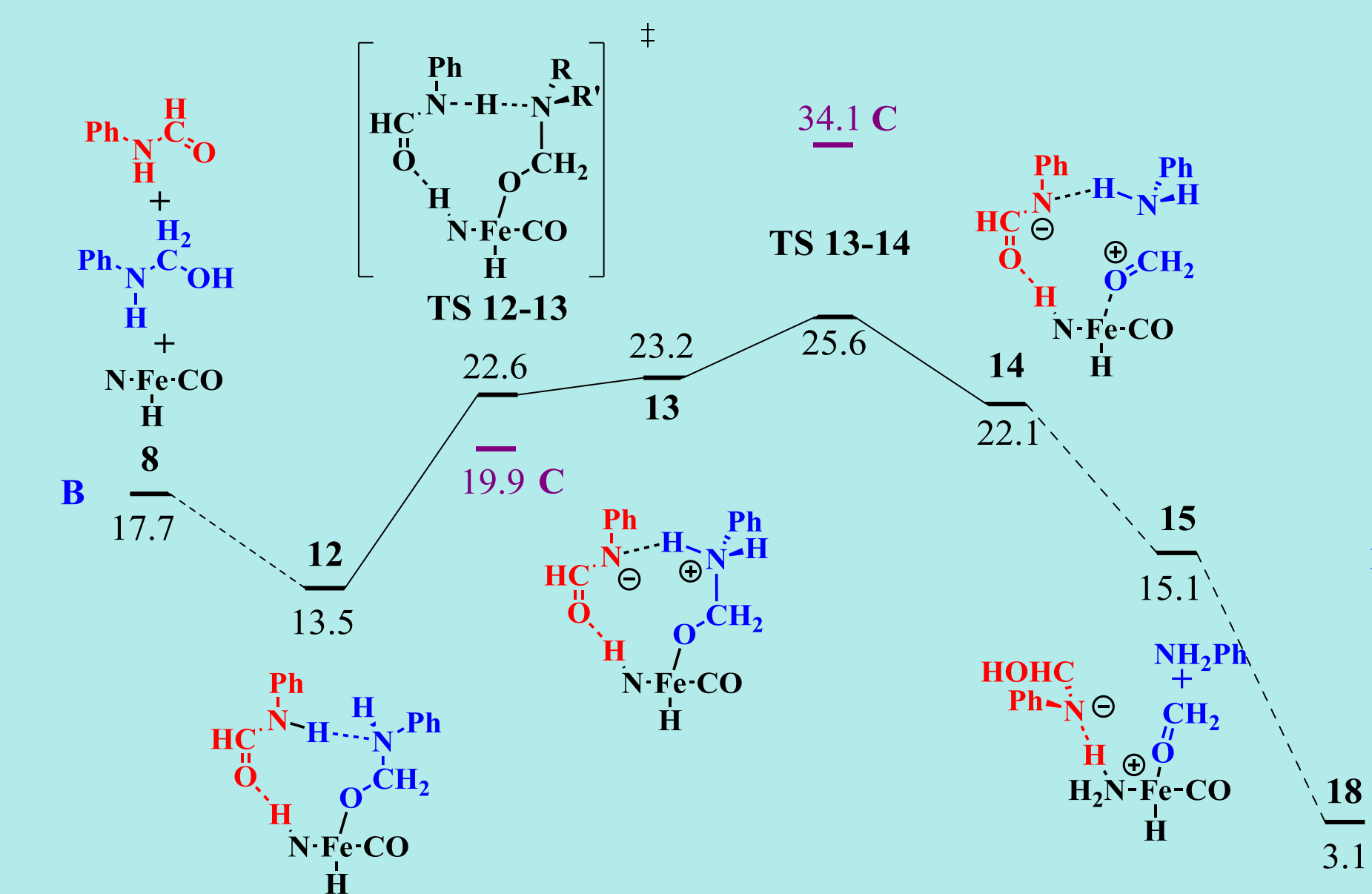
Amides are obtained as intermediate and by-product in the hydrogenation of CO₂ to methanol with a Ru pincer catalyst.^[1] With the idea of improving this process by increasing its selectivity and using an earth-abundant metal catalyst, we have studied the mechanism for the hydrogenation of amides with the Fe-pincer catalyst **A** by DFT methods.



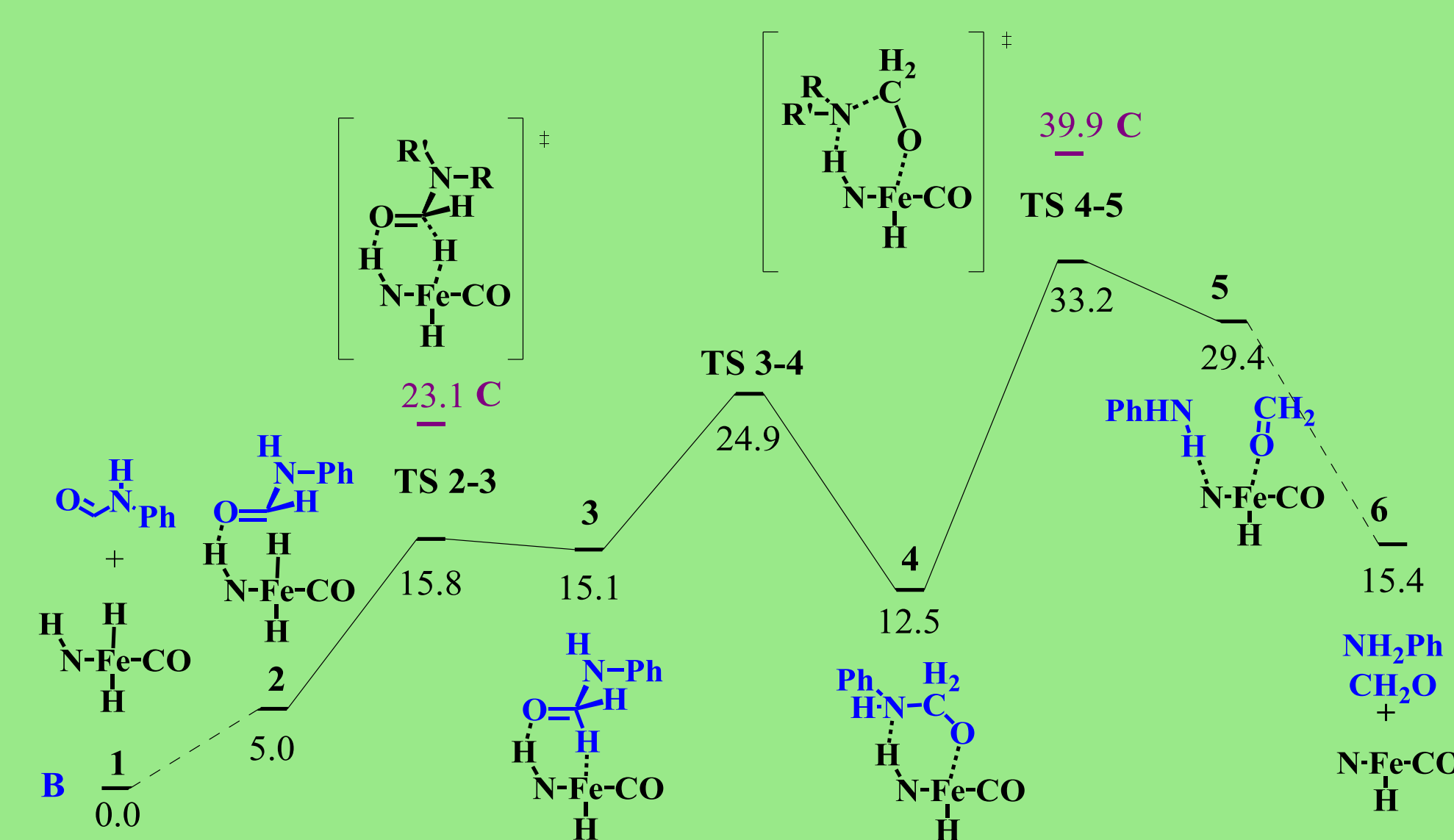
In this reaction, which was recently reported by Profs. Bernskoetter and Hazari,^[2] the conversion of the amide **B** to methanol takes place at 30 atm and 373.15 K in THF, while the amide **C** requires in addition **B** as a co-catalyst. Since the mechanism for the hydrogenation of formaldehyde to methanol has been already reported,^[3] we have focused our computational study in the hydrogenation of an amide to formaldehyde and in the role of the co-catalyst.

Cat-B-Assisted

The protonation and C-N bond cleavage takes place in two steps when the Fe-catalyst and **B** are involved in this process due to the higher acidity of **B** compared to the catalyst. The formation of a zwitterion intermediate favours the C-N bond cleavage. While this step has a higher energy barrier with **C** than with **B**, the protonation follows the opposite trend.

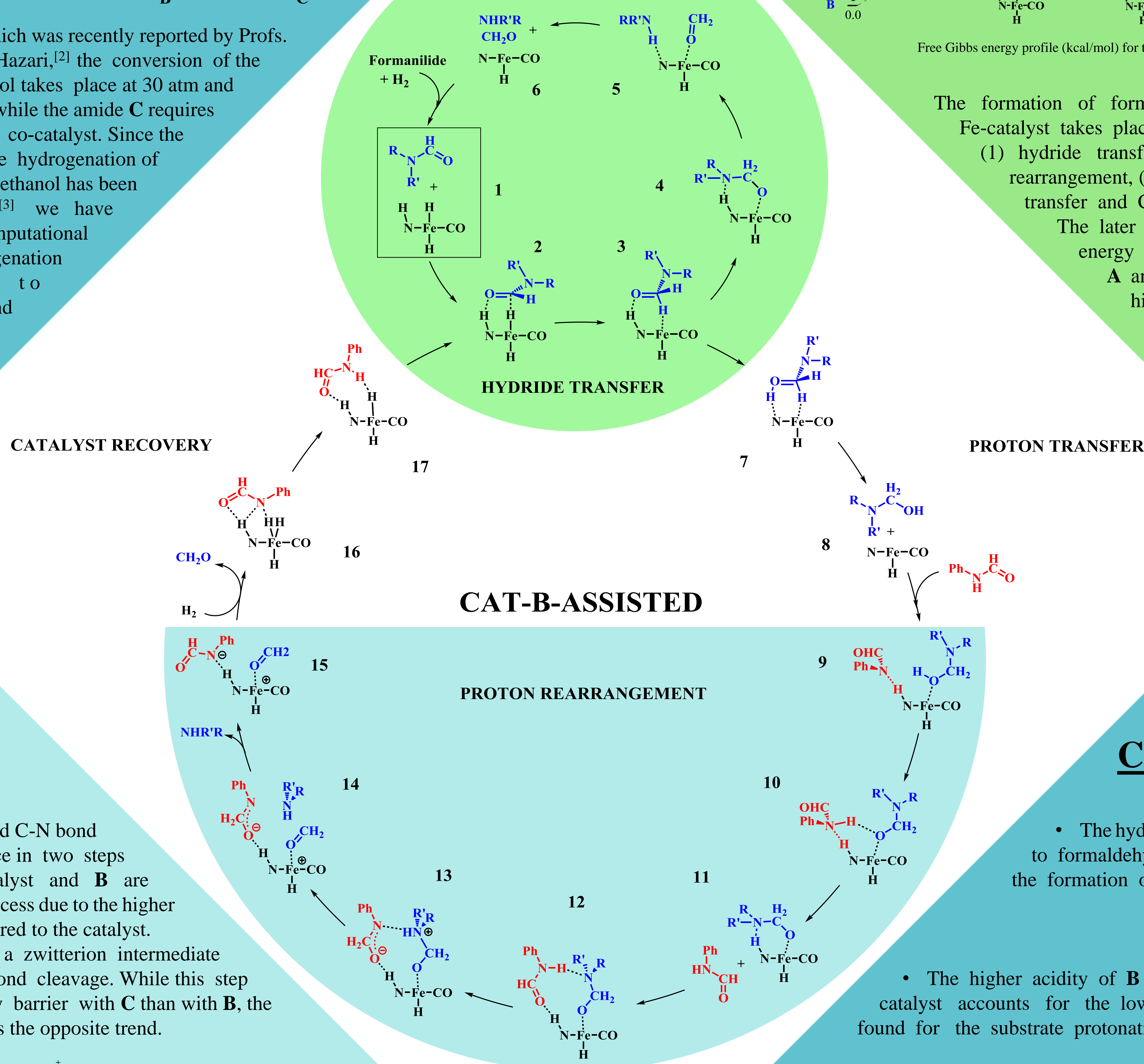


Cat-assisted



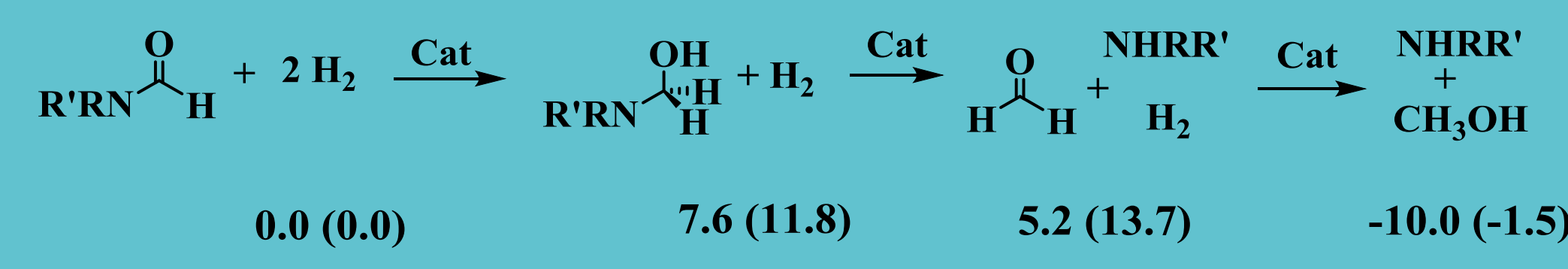
The formation of formaldehyde by the Fe-catalyst takes place in three steps: (1) hydride transfer, (2) geometry rearrangement, (3) concerted proton transfer and C-N bond cleavage. The later step has the highest energy barrier for reactants **A** and **B**, and it is too high to take place at the experimental reaction conditions.

CAT-ASSISTED



Conclusions

- The hydrogenation of amide to formaldehyde is endoergic but the formation of methanol drives the reaction.
- The higher acidity of **B** compared to the catalyst accounts for the lower energy barrier found for the substrate protonation by **Cat-B** than by **Cat**.
- With both **B** and **C** substrates, the highest energy barrier involves the C-N bond cleavage.



Thermodynamics (in kcal/mol) for the conversion of **B** and **C** to methanol

Computational details: Geometry optimizations were performed with the M06 functional and a LANL2DZ (for Fe) and 6-31+G (for the rest of atoms) basis set. Free Gibbs energies were calculated at 30 atm and 373.15 K, using THF (SMD) as solvent. Energies were refined with triple z basis set analogs.