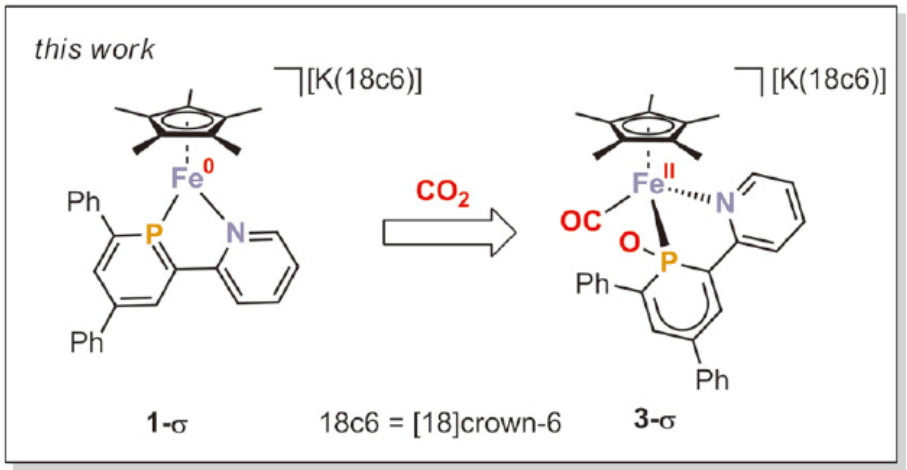
Literature Report ICC Report V

A Facile $C{=}O$ Bond Splitting of CO_2 Catalyzed by Phosphinine Iron(0) Complex



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December 25, 2019

Contents

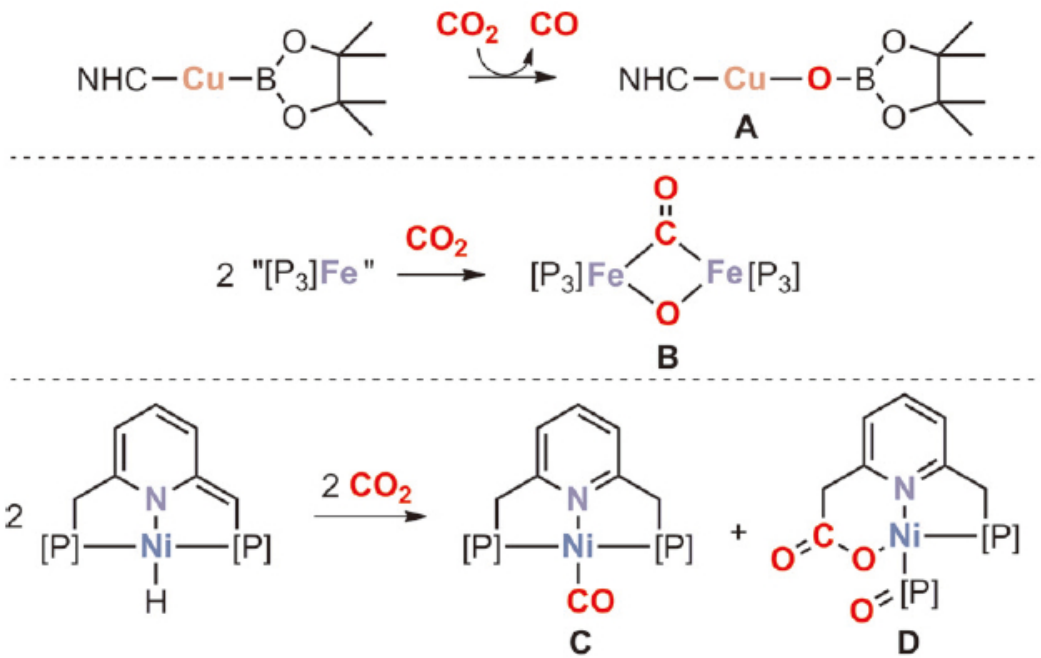
Background

$\mathrm{C{=}O}$ Bond Splitting of $\mathrm{CO_2}$ has become established for some d-block metals (Ti, Zr, W, Ir) and f-block metals (U).

However, the use of earth-abundant 3d metals remains surprisingly under-explored, particularly given the role that such metals play in biological $\mathrm{CO_2}$ reduction to CO, mediated by Ni, Fe CO dehydrogenase.

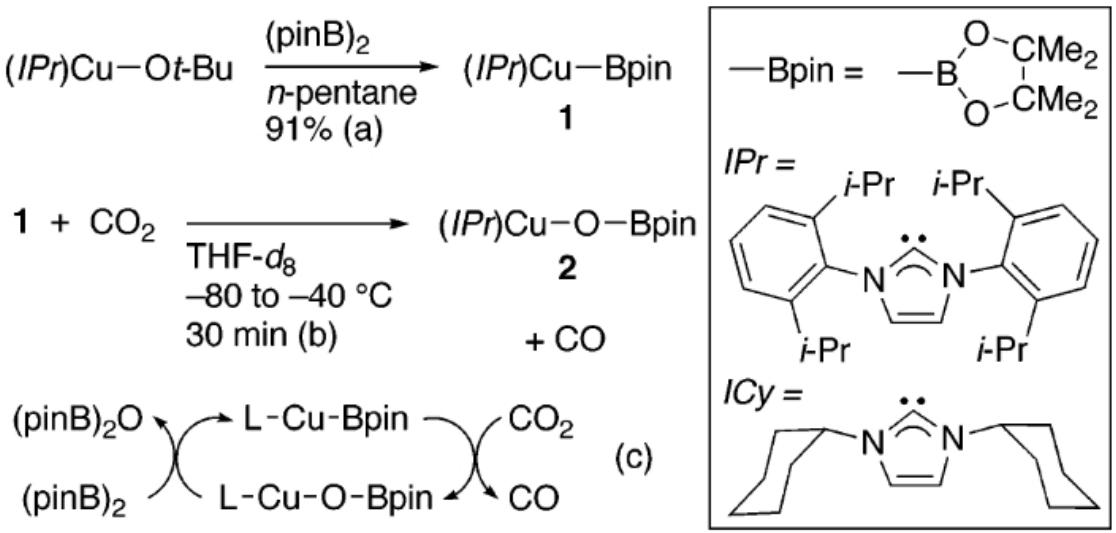
Background

Previous examples of CO_2 cleavage based on 3d metals



Laitar, D. S. et al. *J. Am. Chem. Soc.* **2005**, *127*, 17196–17197
Sadique, A. R. et al. *Inorg. Chem.* **2008**, *47*, 784–786
Oren, D. et al. *Organometallics* **2018**, *37*, 2217–2221

The research of D. Laitar et al. provides a catalytic cycle for CO_2 deoxygenation. ICy-cooper catalysis gives 100 turnovers in 1h.



Laitar, D. S. et al. *J. Am. Chem. Soc.* **2005**, *127*, 17196–17197

This work is the first reported example of $\mathrm{C{=}O}$ cleavage of a $\mathrm{CO_2}$ molecule mediated by a single Fe centre.

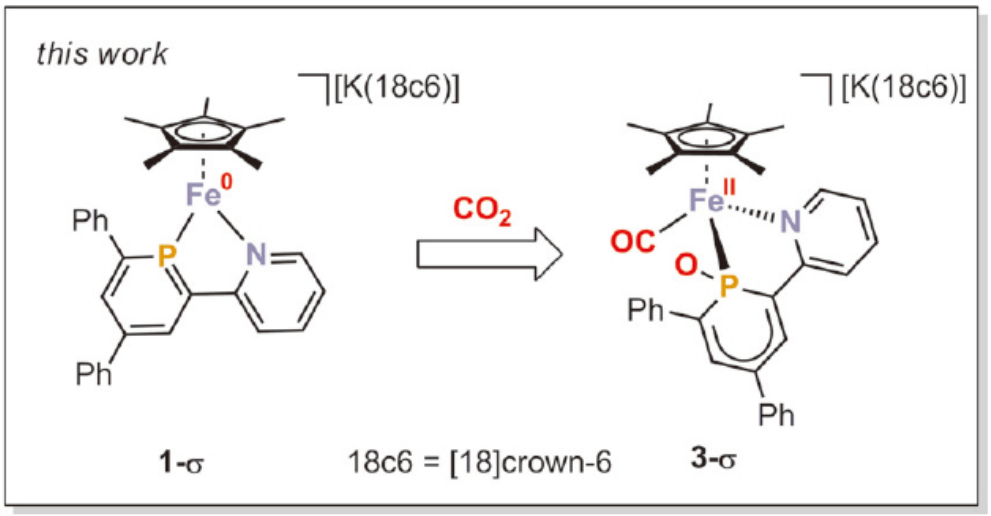


Figure 1: Leitl, J. et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 15407–15411

Inspiration

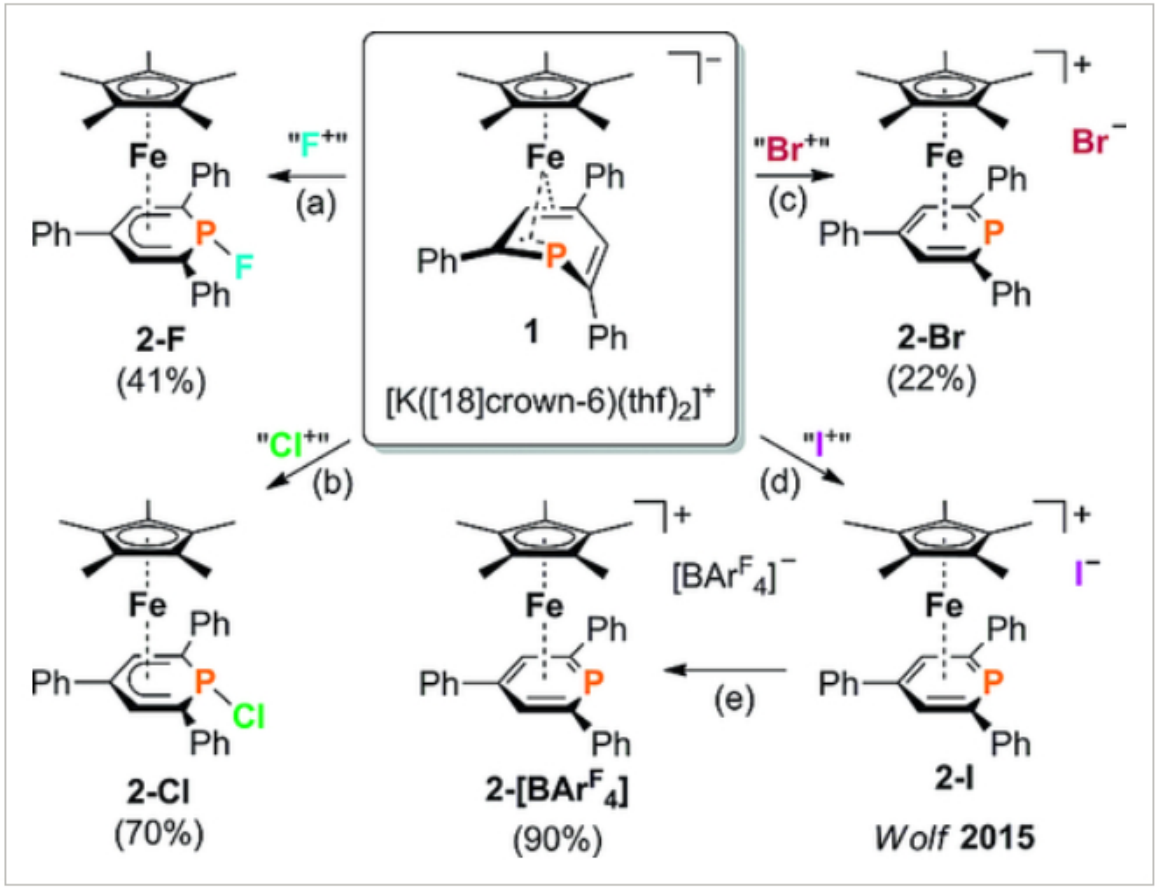


Figure 2: [Cp*Fe(η^4-TPP)] and derived compounds
Hoidn, C. M. et al. *Eur. J. Inorg. Chem.* **2019**, *2019*, 1567–1574

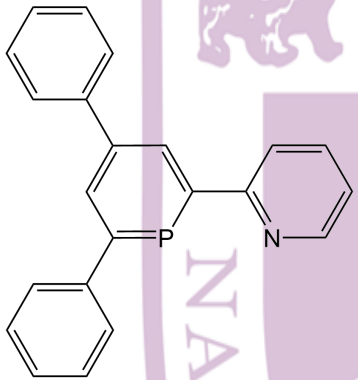


Figure 3: New ligand 2-(2'-pyridyl)-4,6-diphenylphosphinine

Preparation

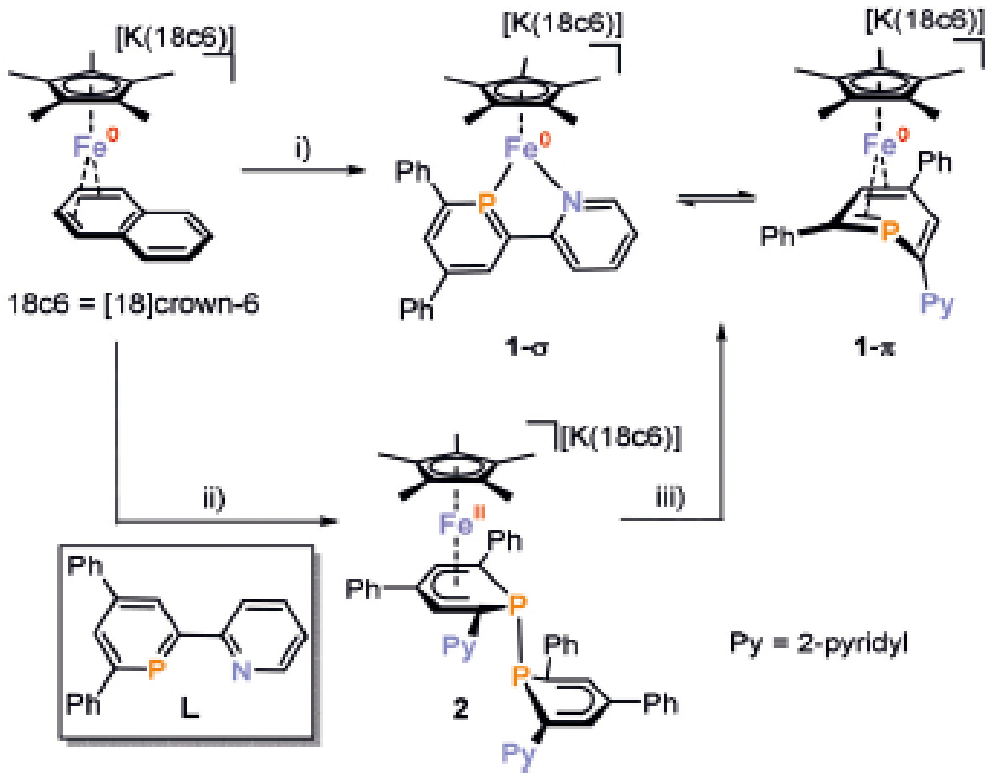


Figure 4: i) L, DME, -35□to RT, -naphthalene;
ii) 1 equiv. [K([18]crown-6)][Cp*Fe-($C_{10}H_8$)], 2 equiv. L, toluene/THF, -35□to RT;
iii) 1 equiv. [K-([18]crown-6)][Cp*Fe($C_{10}H_8$)], THF.

Calculation for 1-σ/1-π

Conversion of 1-π to 1-σ is calculated to proceed with a barrier of 27.0 kcal / mol, consistent with an equilibrium at room temperature. NMR indicates an approximately 2:1 ratio of 1-σ:1-π.

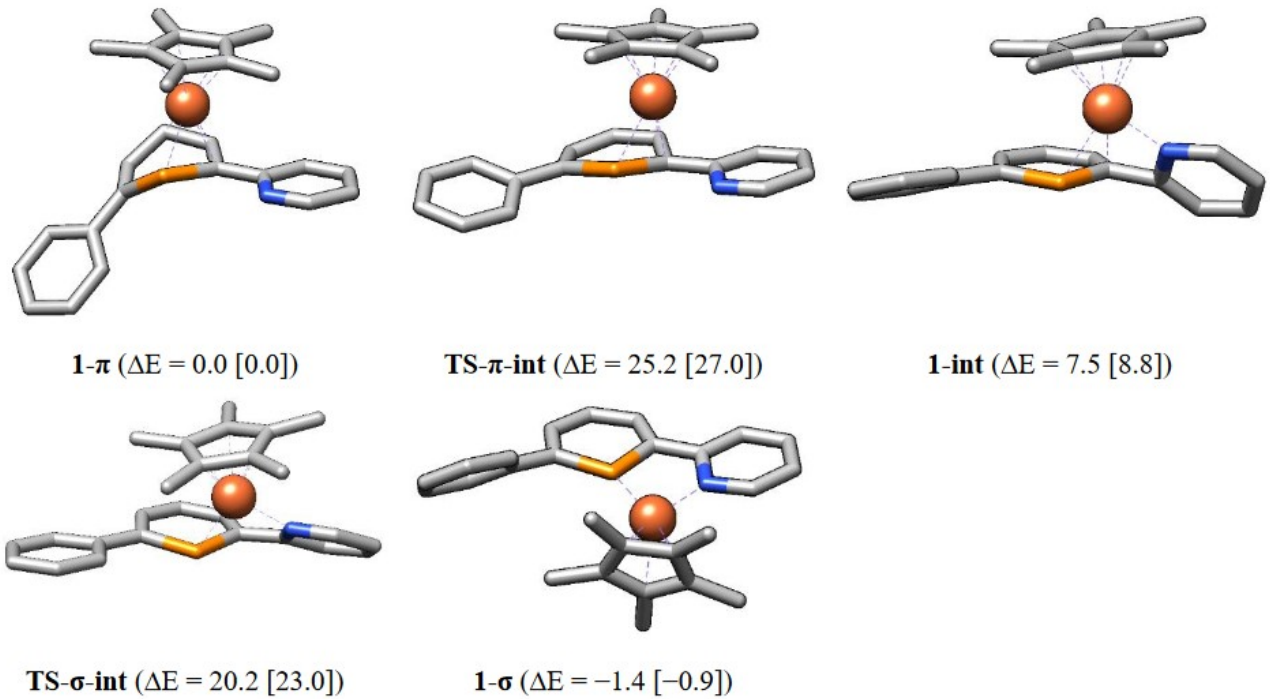


Figure 5: Calculation results at TPSSh-D3/def2-TZVP. The geometry is optimized at BP86/def2-TZVP. Both are carried in THF solvent with CPCM model

Splitting Reaction

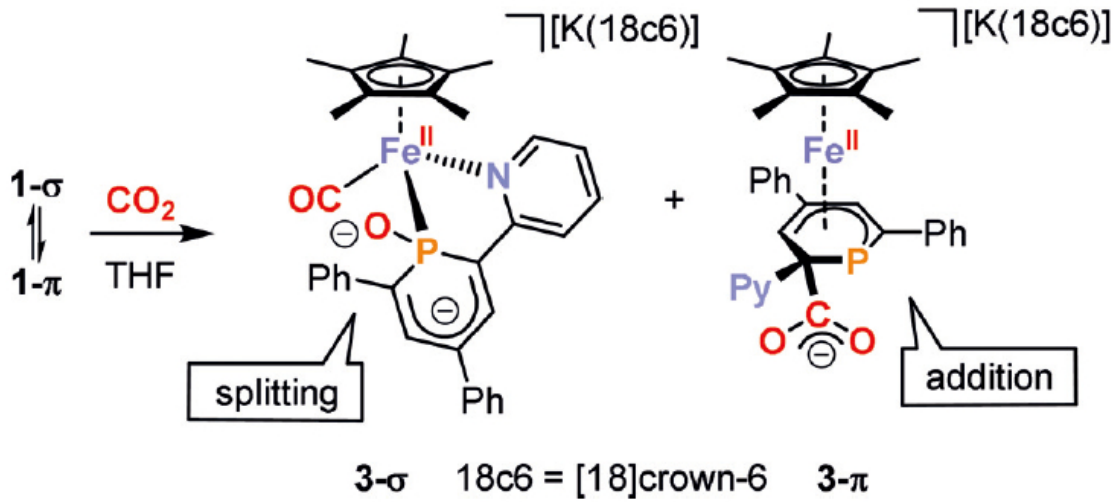
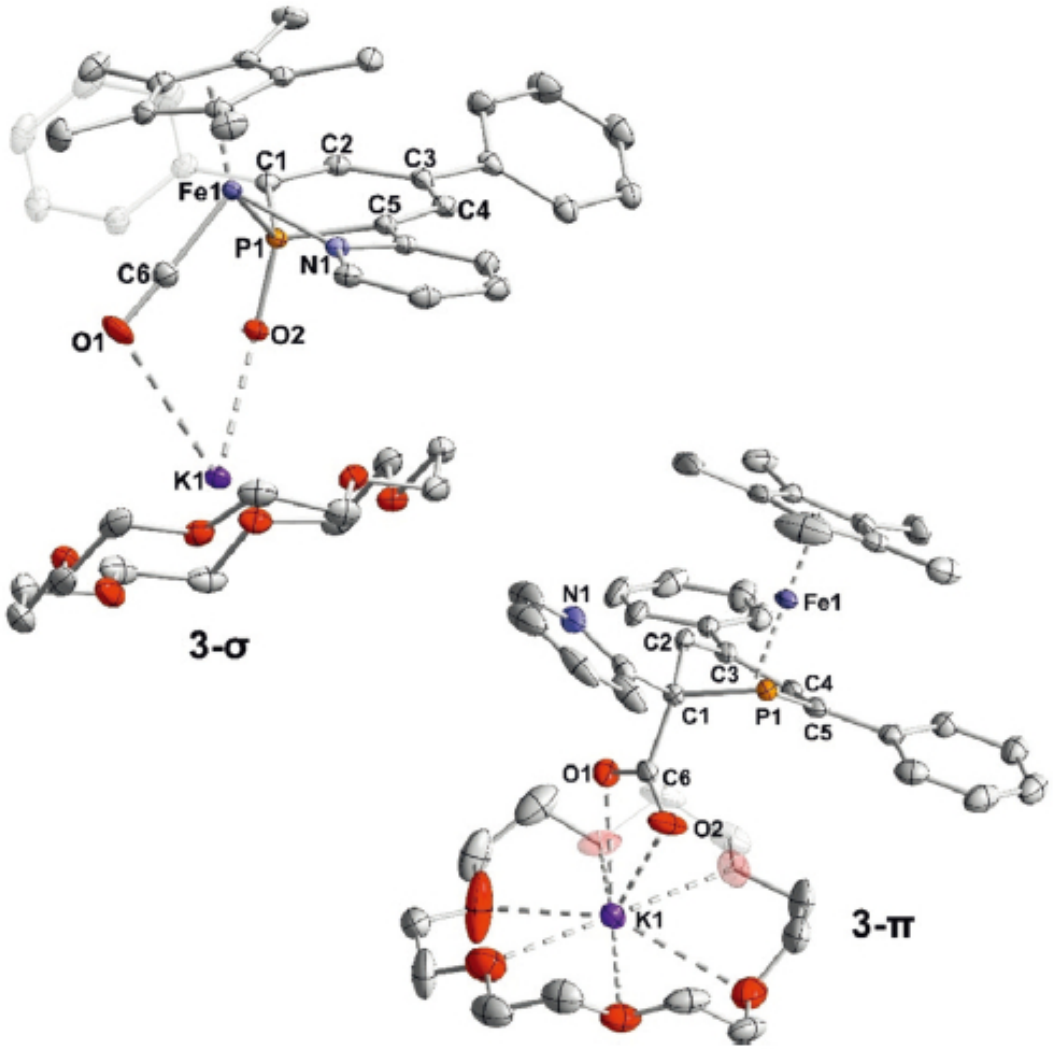


Figure 6: Reaction of 1-σ and 1-π with CO_2 (1 atm) in THF at room temperature.

Solid state structures of 3-σ and 3-π



Calculation for 1 $\rightarrow$ 3 Reaction

Very small energy barriers:

- 1-σ -> 3-σ: 3.5 kcal / mol
- 1-π -> 3-π: 5.5 kcal / mol

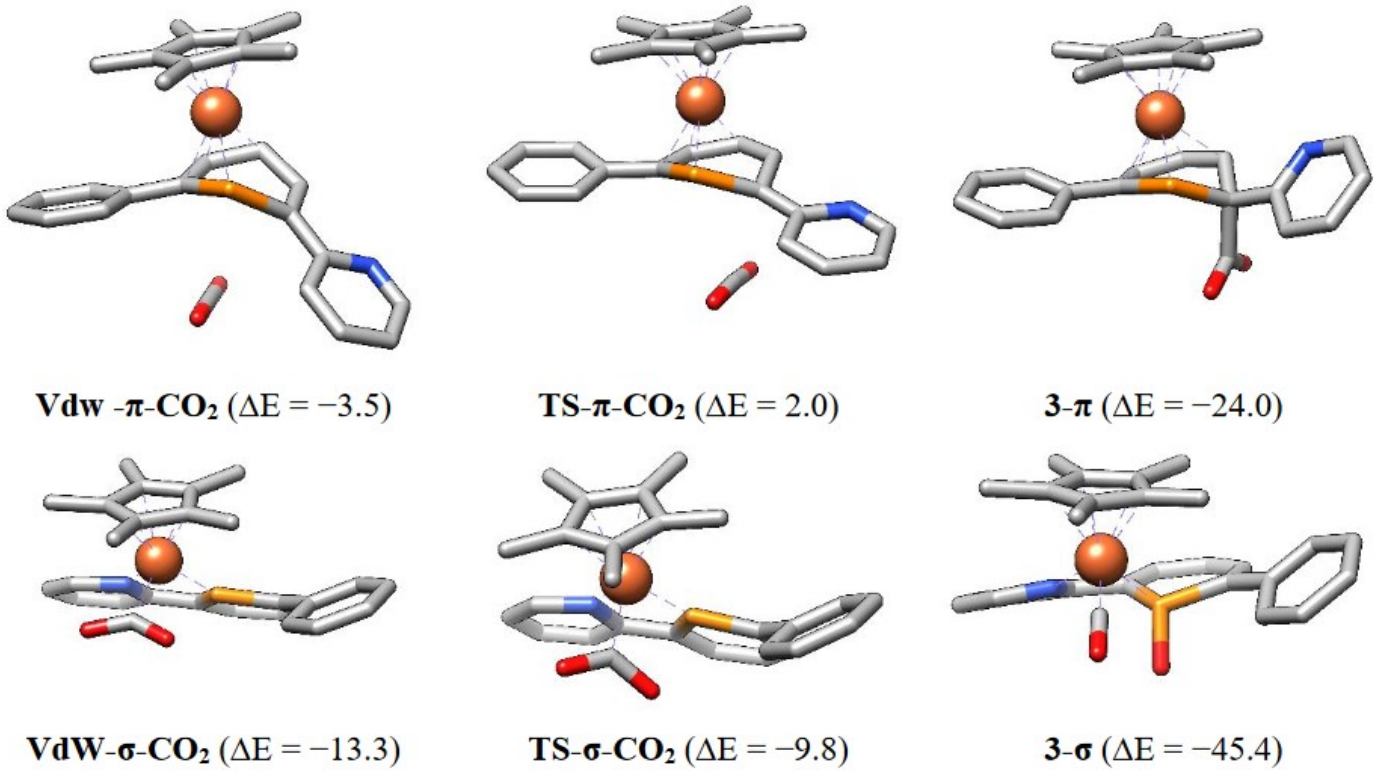


Figure 7: Calculation results at TPSSh-D3/def2-TZVP. The geometry is optimized at BP86/def2-TZVP. Both are carried in THF solvent with CPCM

Discussion and Expectations

- Full catalysation cycle
- Diversification of 1-σ
- Orbital analysis

Current Progress

Testing calculation with ORCA

method	basis	cores	time
PBE0-D3	def2-TZVP/def2-SVP (1758)	24	12h (40 cyc)
PWPB95-D3	def2-TZVPP (2583)	72	29m
DLPNO-CCSD(T)	def2-TZVPP (2583)	30	18.5h

Where, RI-J and RIJCOSX used for DFT, RI-MP2 used for Double-hybrid DFT.
DLPNO is performed at NormalPNO level. TightPNO calculation is on running for 3 days.