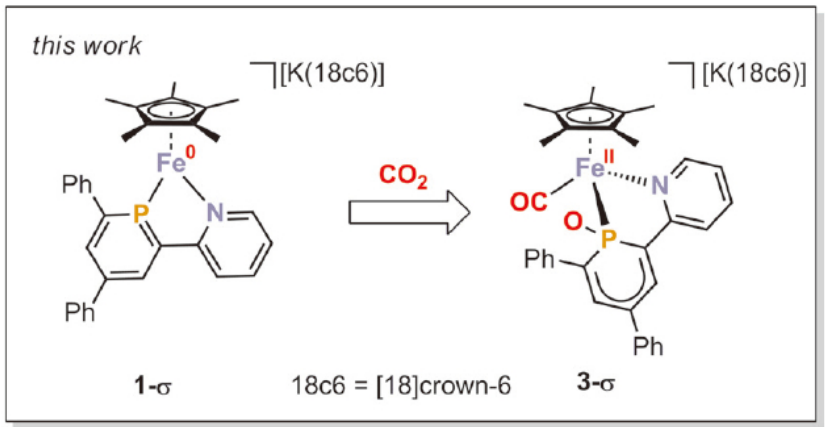
Literature Report: A Facile $C{=}O$ Bond Splitting of CO_2 Catalyzed by Phosphinine Iron(0) Complex



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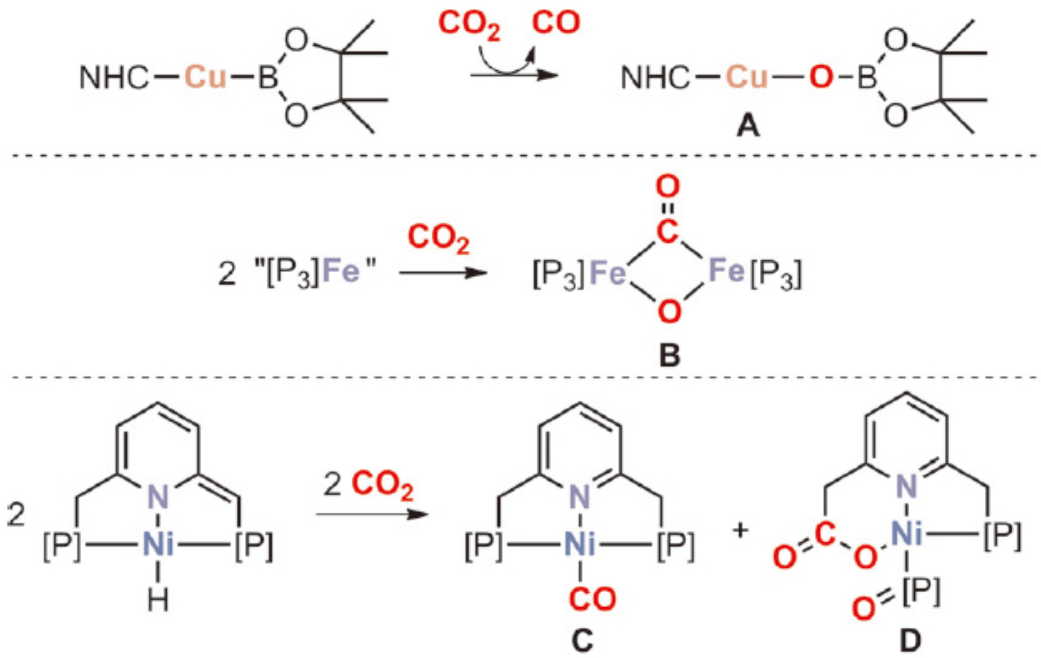
Contents

Background

$\mathrm{C{=}O}$ Bond Splitting of $\mathrm{CO_2}$ has become established for early 3d metals and f-block metals.
In comparison, the use of earth-abundant late 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. *Journal of the American Chemical Society* **2005**, *127*, 17196–17197
Sadique, A. R. et al. *Inorganic chemistry* **2008**, *47*, 784–786
Oren, D. et al. *Organometallics* **2018**, *37*, 2217–2221

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

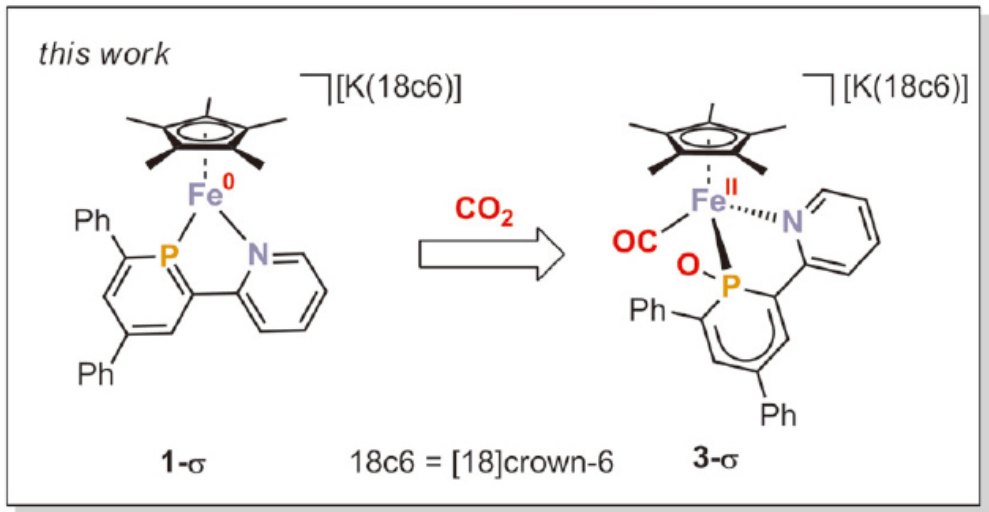


Figure 1: Leitl, J. et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 15407–15411

Inspiration

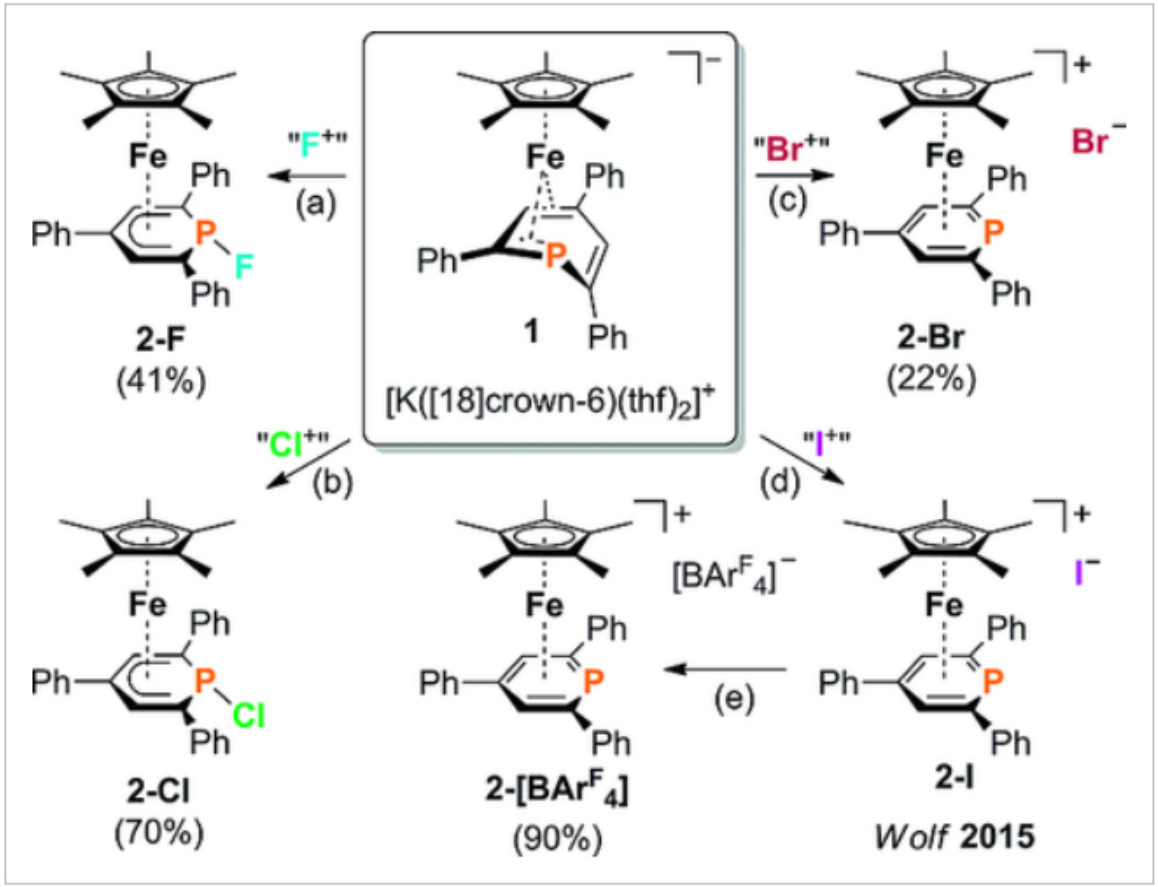


Figure 2: [Cp*Fe(η^4-TPP)] and derived compounds
Hoidn, C. M. et al. *Eur. J. Inorg. Chem.* **2019**, *2019*, 1567–1574

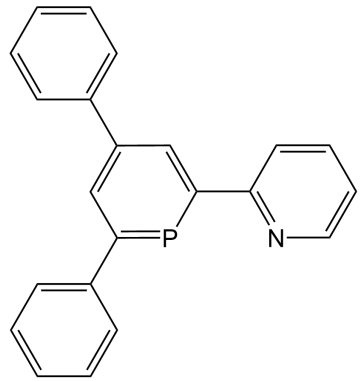


Figure 3: New ligand 2-(2'-pyridyl)-4,6-diphenylphosphinine

Preparation

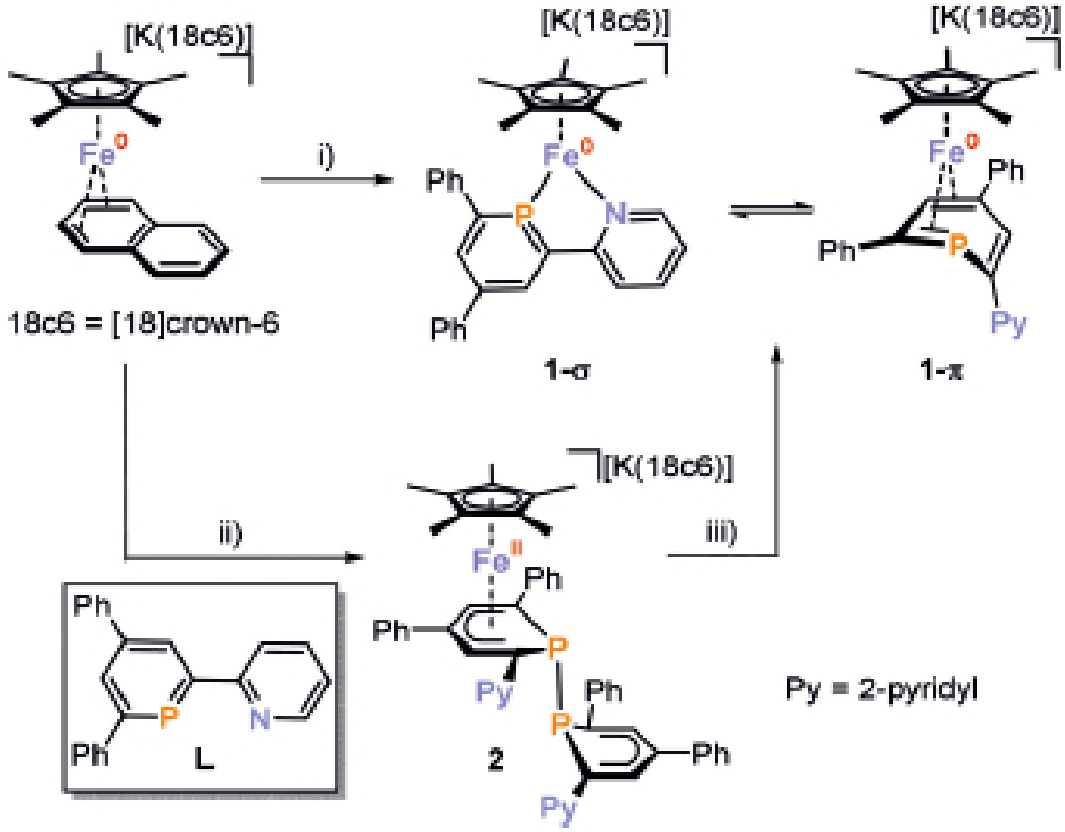


Figure 4: i) L, DME, -35°Cto RT, -naphthalene; ii) 1 equiv. [K([18]crown-6)][Cp*Fe-($C_{10}H_8$)], 2 equiv. L, toluene/THF, -35°Cto RT; iii) 1 equiv. [K-([18]crown-6)][Cp*Fe($C_{10}H_8$)], THF.

Solution-phase ^{31}P NMR spectrum shows 1-σ and 1-π, while XRD and ^{31}P CP MAS show only 1-σ. Selective crystallization failed.

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.

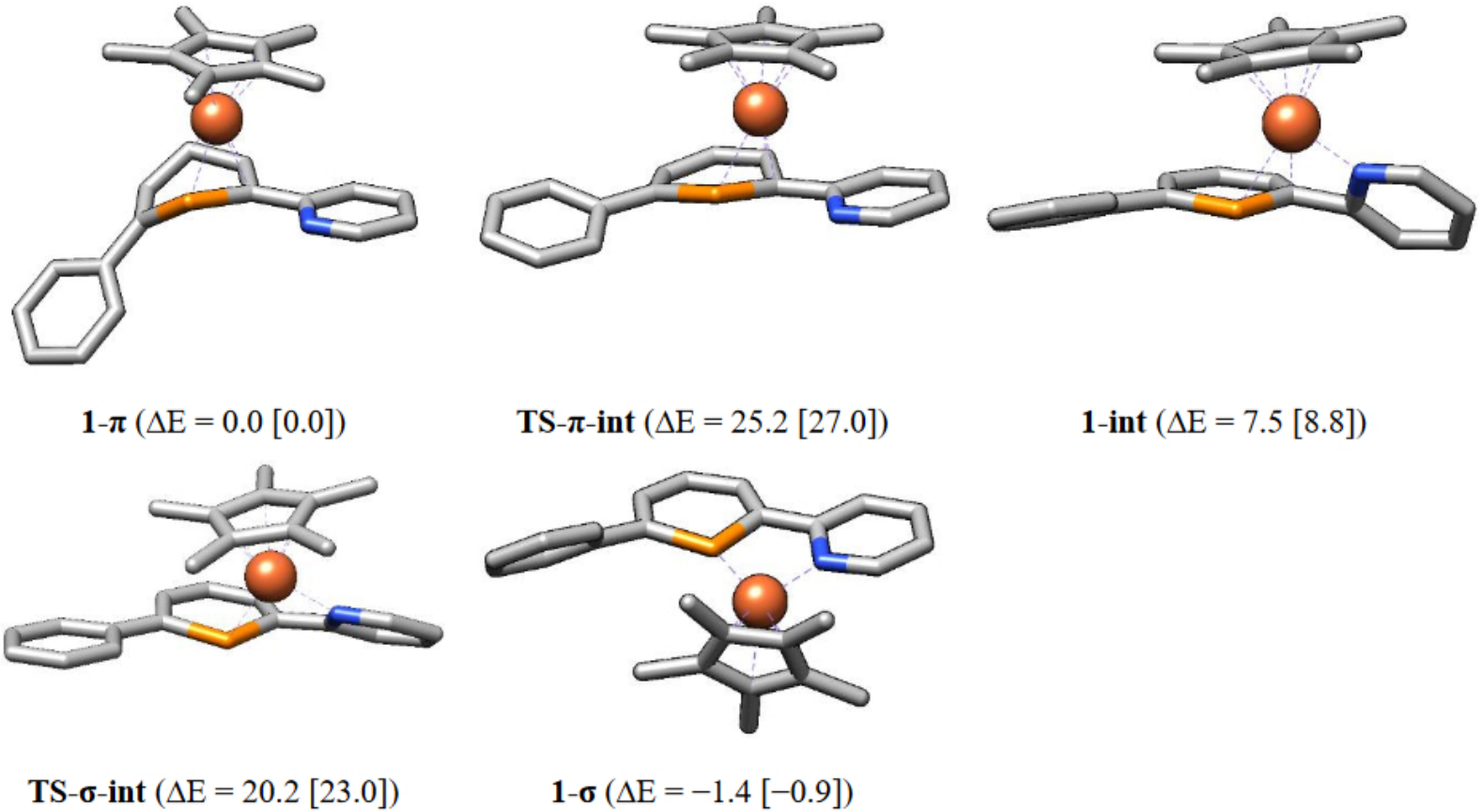


Figure S33 - Optimised structures for the isomerisation of **1-π to 1-σ**. Energies are given in kcal·mol^{-1} relative to the optimised structure of **1-π**. Energies in brackets correspond to electronic energies with solvent correction (TPSSh-D3BJ/def2-TZVP CPCM(THF)).

Splitting Reaction

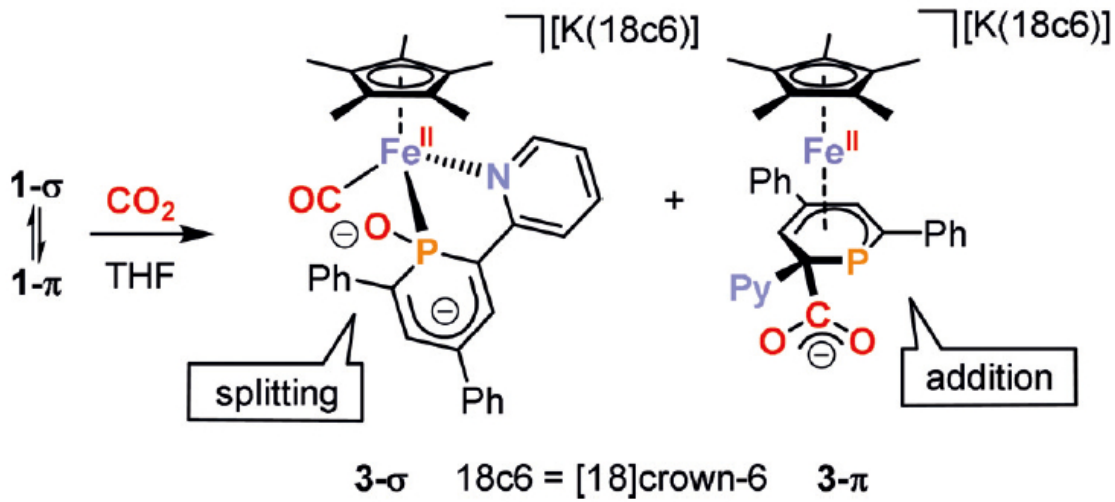
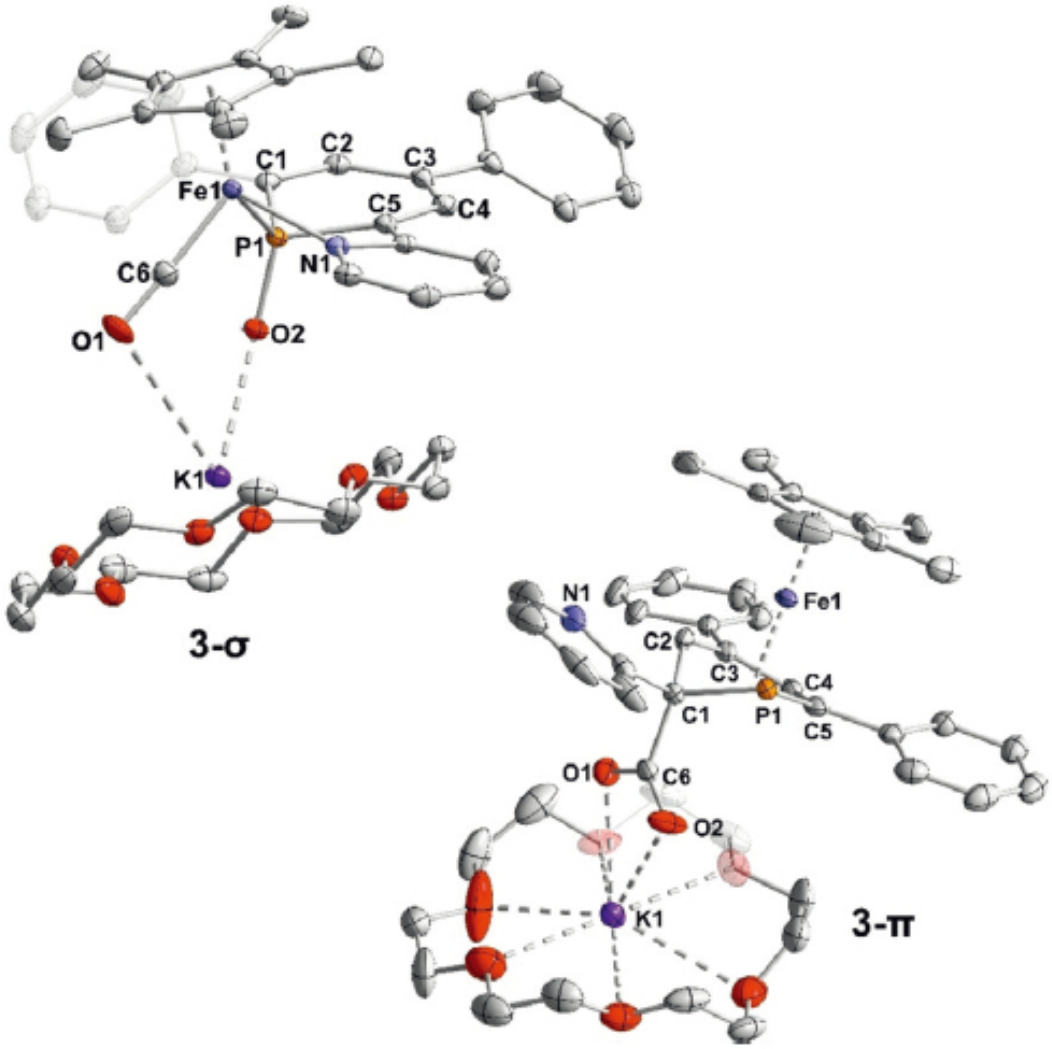


Figure 5: Reaction of 1-σ and 1-π with CO_2 (1 atm) in THF at room temperature.

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

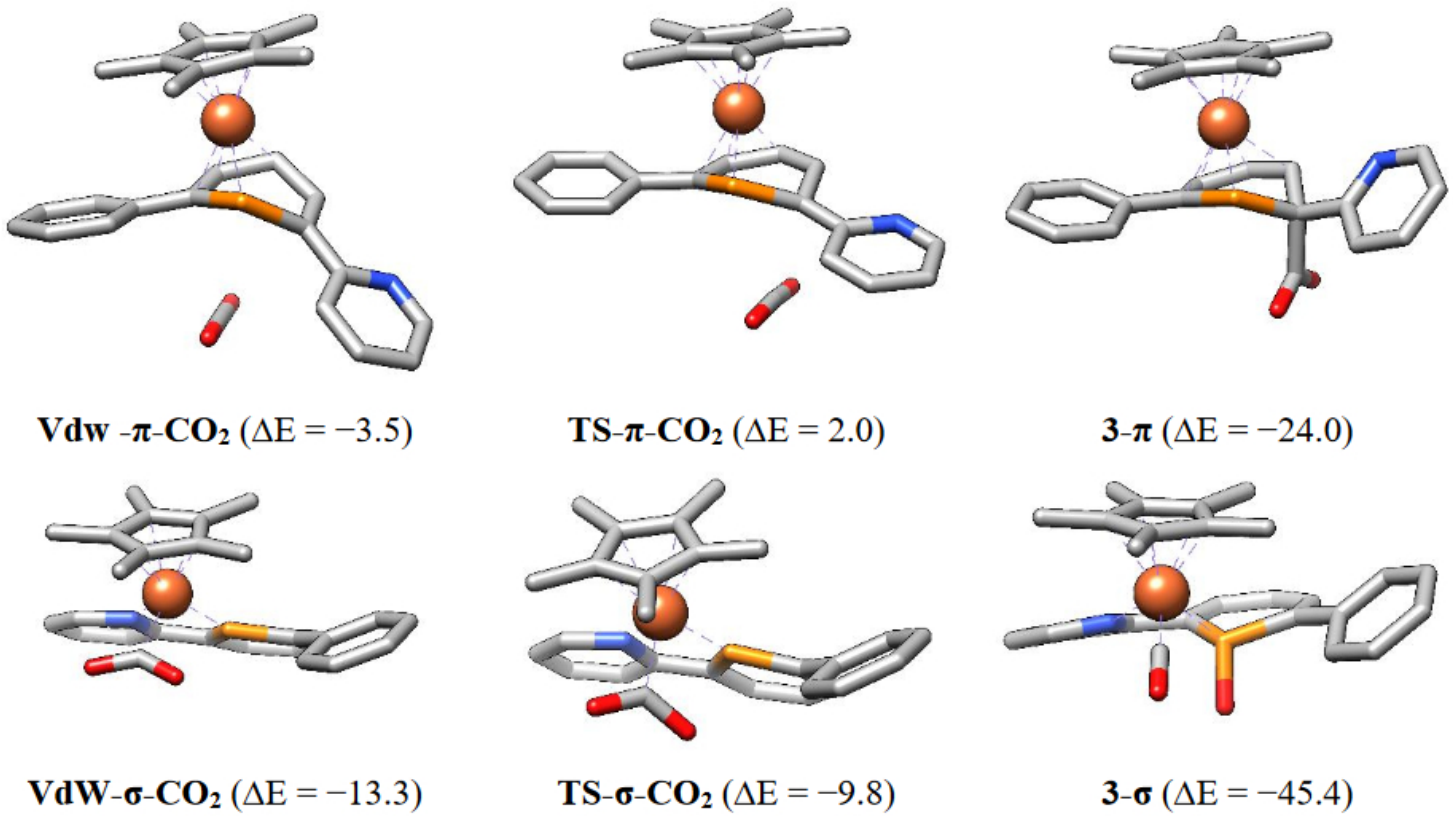


Figure S37 - Optimised key structures for the activation of CO_2 by **1-π** (top) and **1-σ** (bottom). Energies are given in kcal·mol^{-1} relative to the sum of the electronic energies of CO_2 and the relevant isomer of **1**.

Discussion and Expectations

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