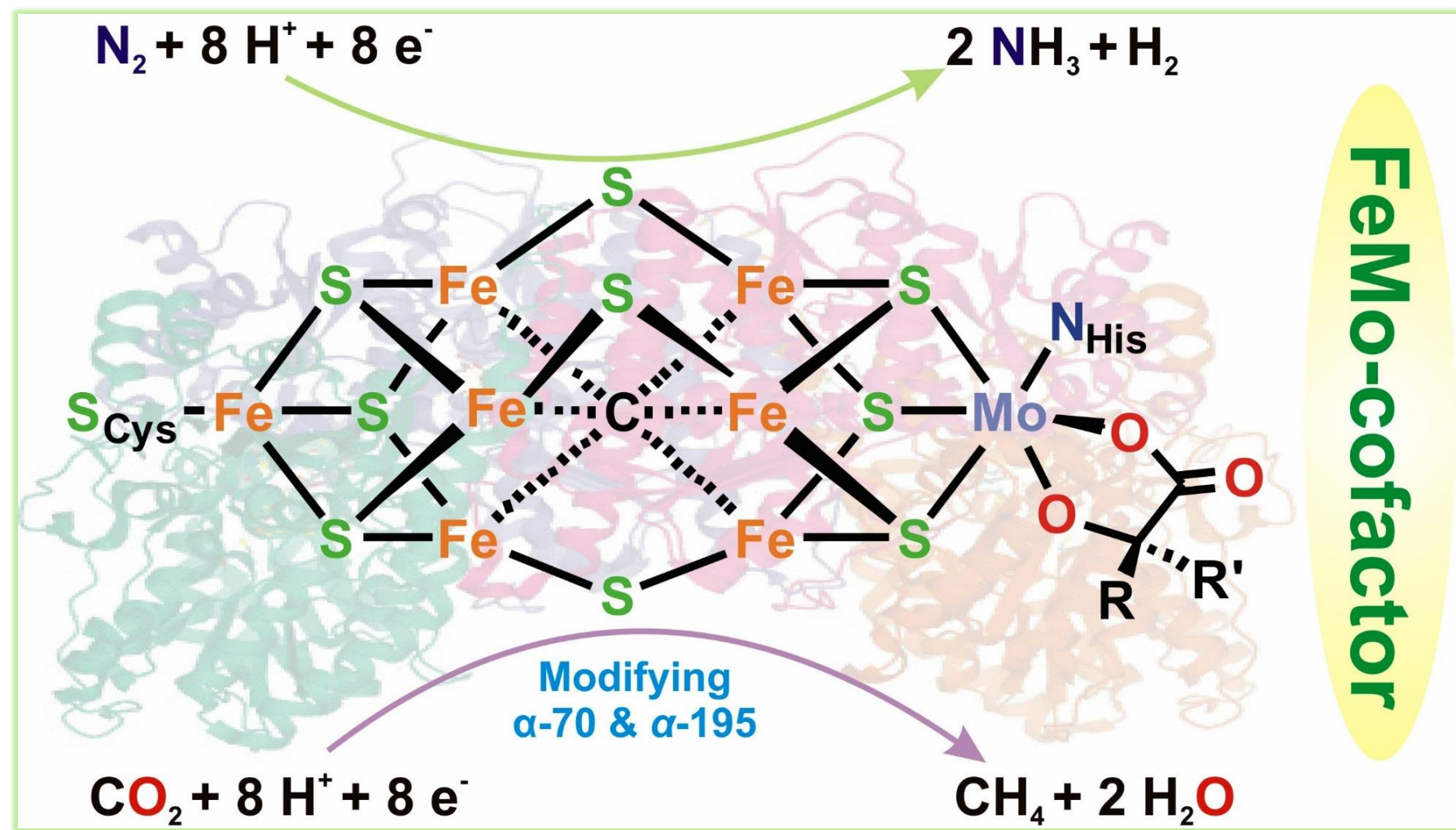


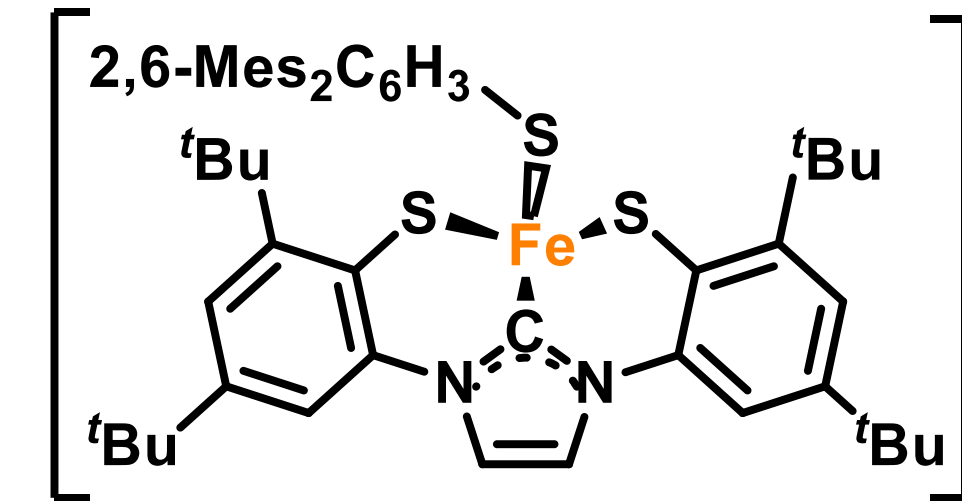
Nitrogenase Enzyme



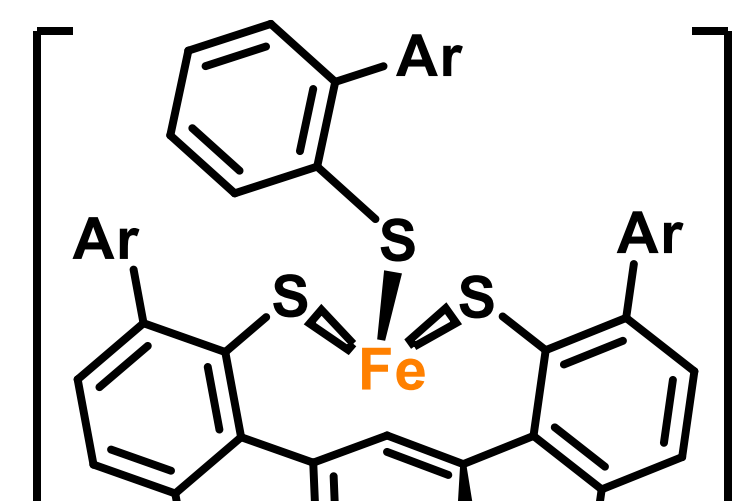
FeMo-cofactor

Fe_7MoS_9C center (FeMo-cofactor) contains the active site of nitrogen fixation responsible for the Nitrogen (N_2) reduction into Ammonia (NH_3).

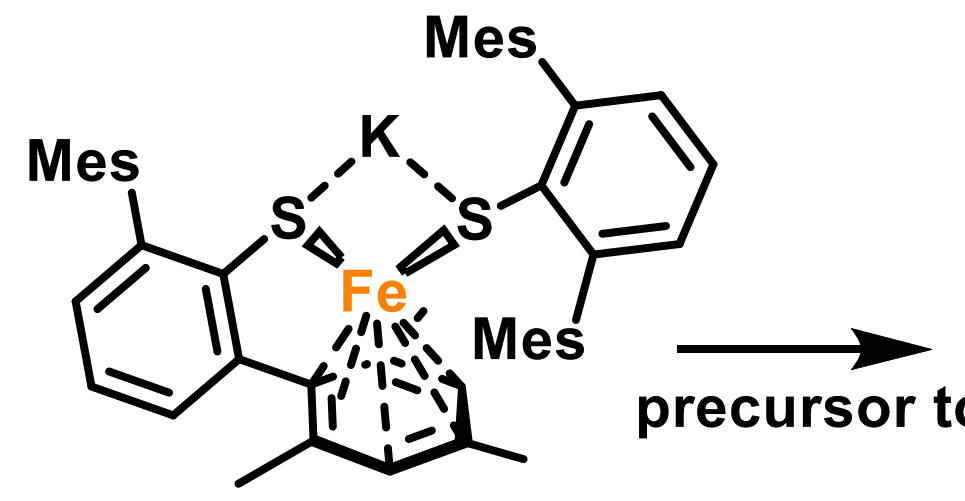
A simple modification in the secondary coordination sphere (amino acids) of the FeMo-co can transform Carbon dioxide (CO_2) into Methane (CH_4).



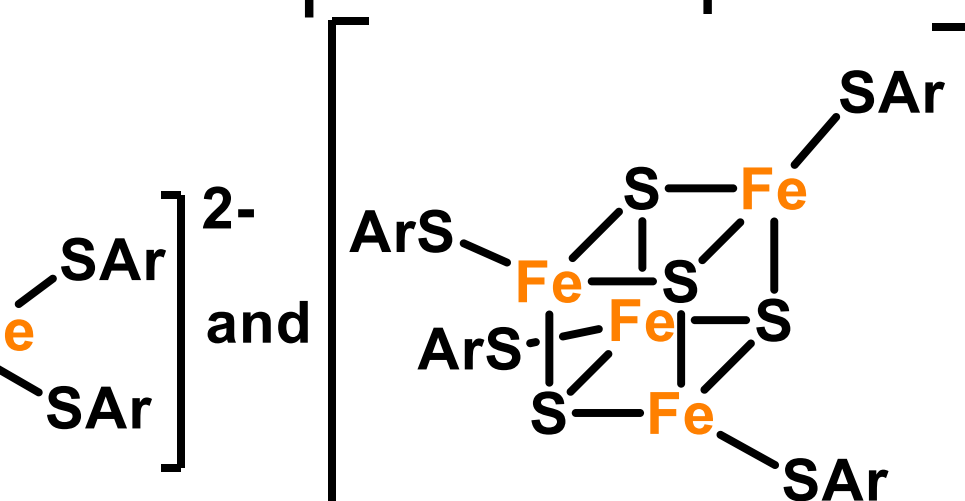
✓ Carbon
✓ Sulfur
✗ Polymetallic
✗ Evolutive



✓ Carbon
✓ Sulfur
✗ Polymetallic
✗ Evolutive

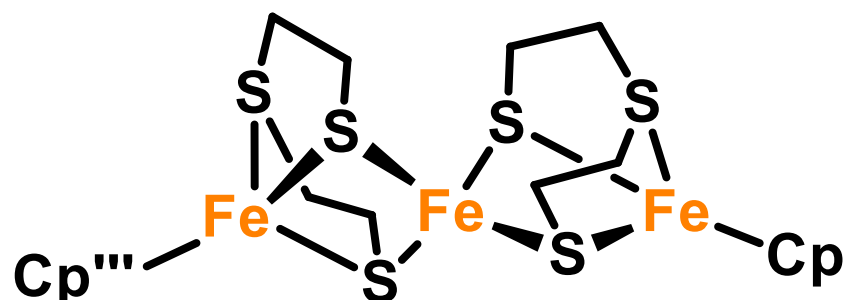


precursor to



✗ Carbon
✓ Sulfur
✓ Polymetallic
✓ Evolutive

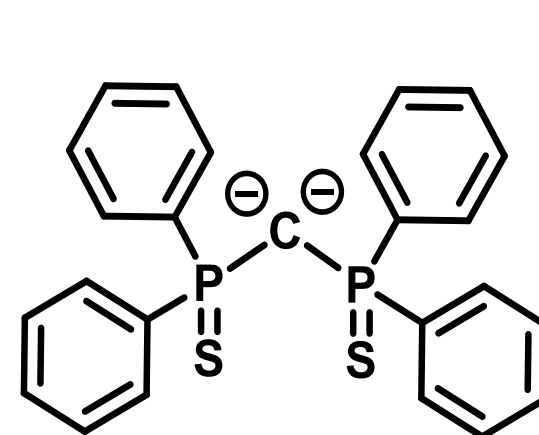
$n=0,1,2,3,4$ $Ar=C_6H_3(2,4,6-Me_3C_6H_2)_2$



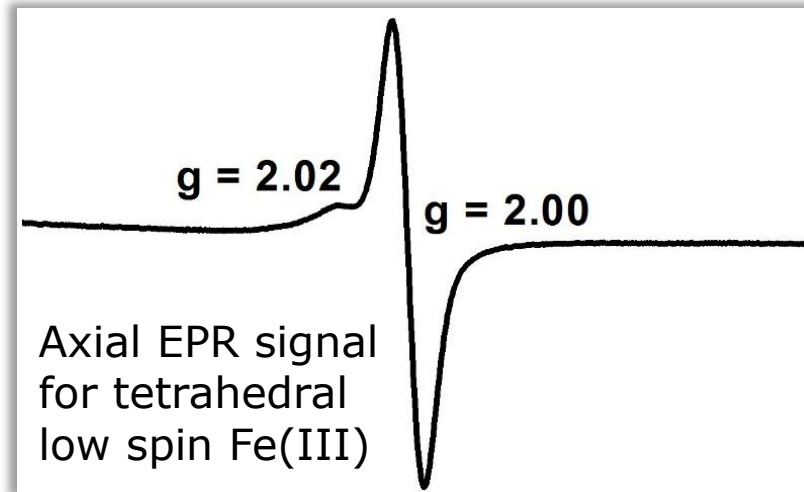
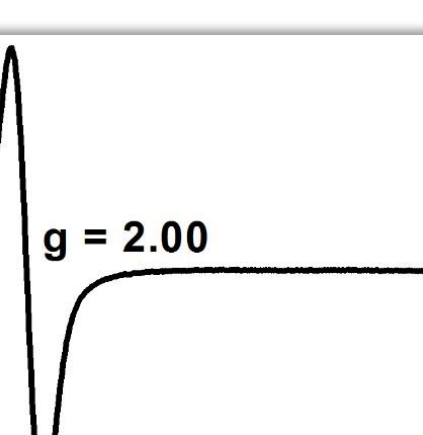
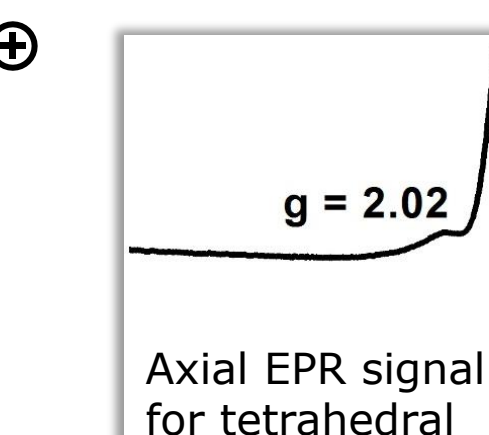
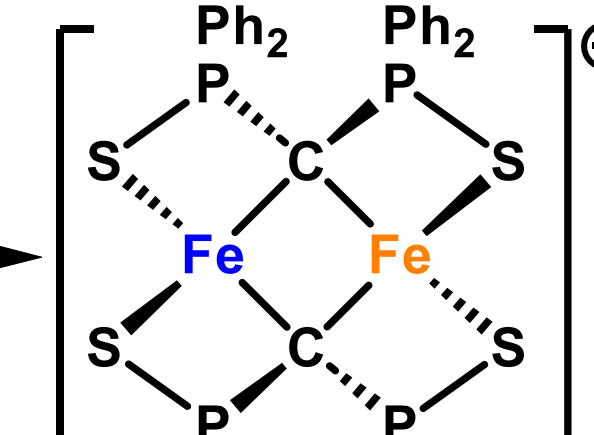
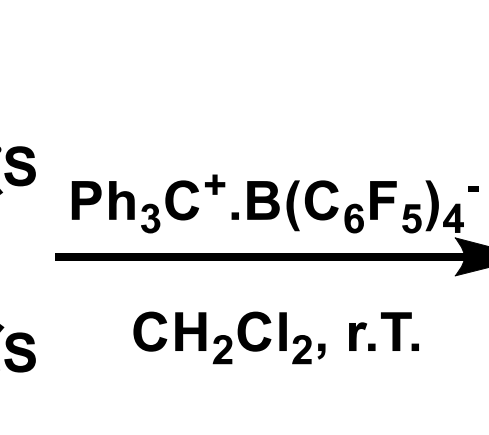
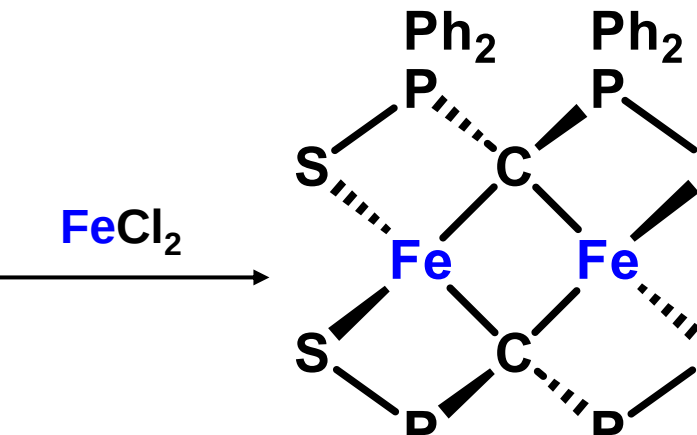
✗ Bridging Carbon
✓ Sulfur
✓ Polymetallic
✓ Evolutive

✓ Catalyses N_2 reduction to $N(TMS)_3$ (TON 25)

Diiron Complexes



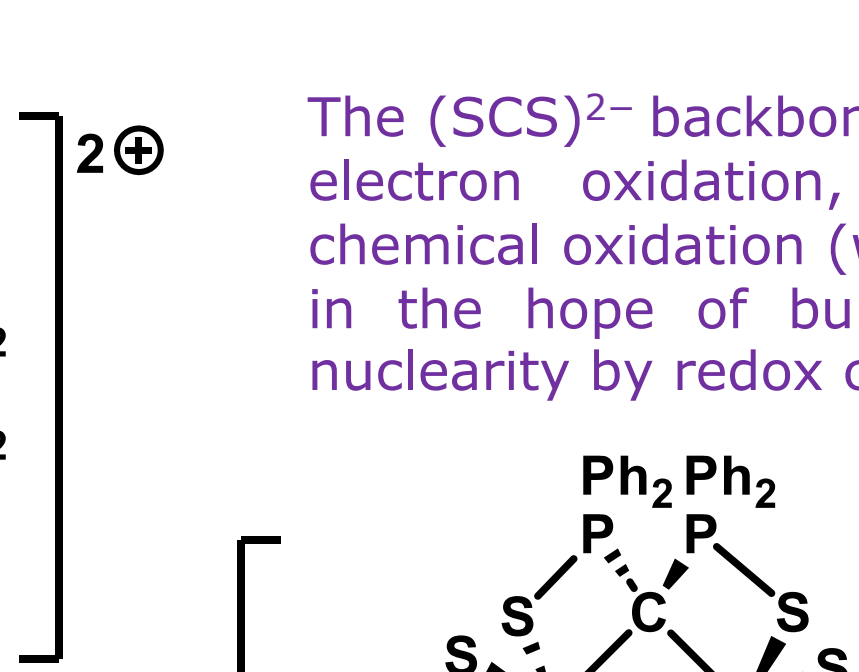
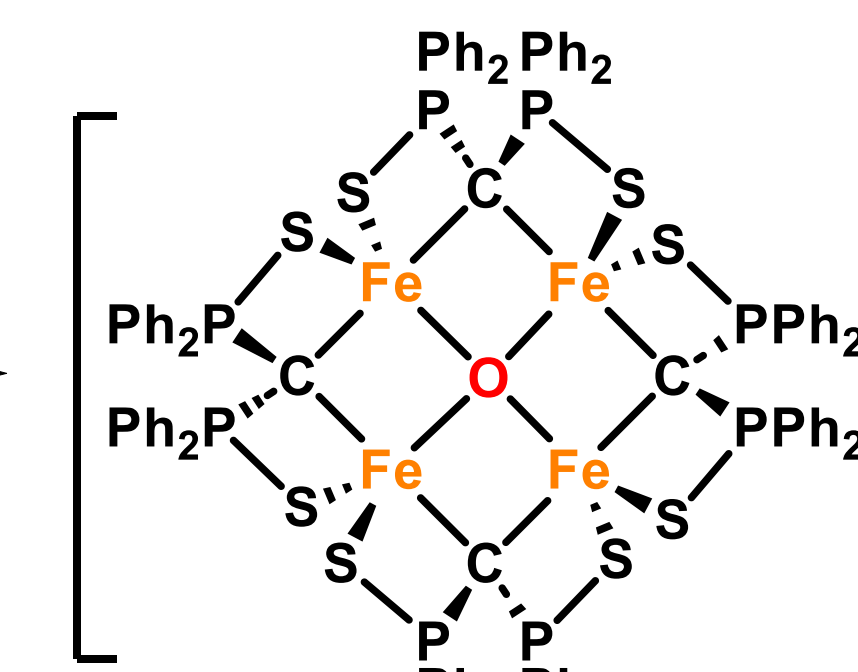
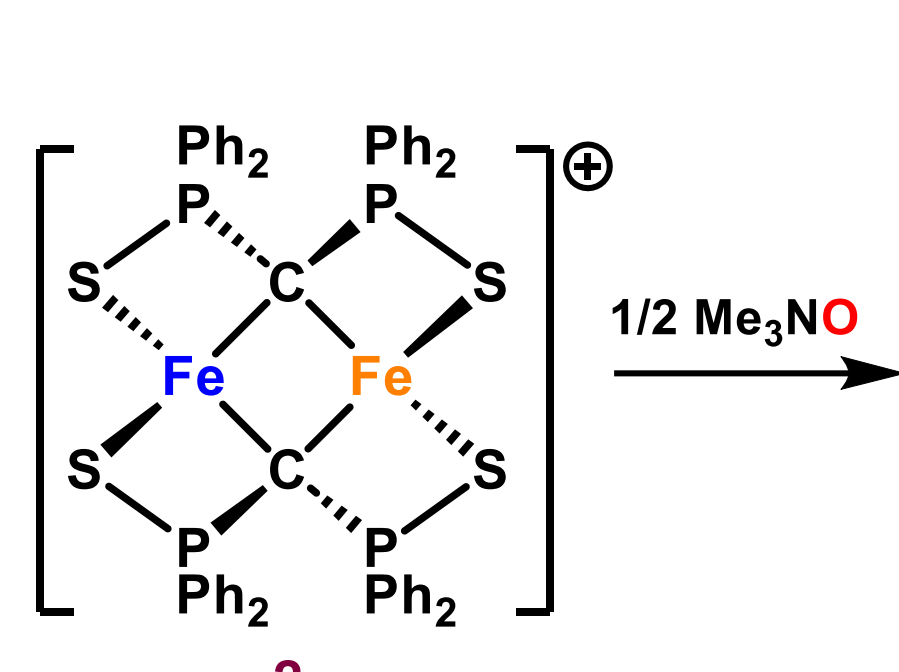
Geminal Dianion



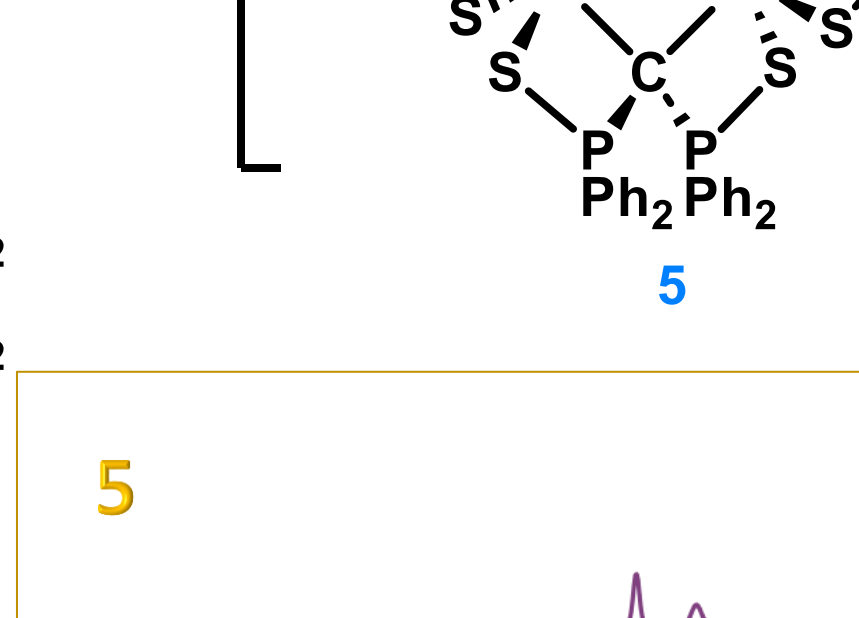
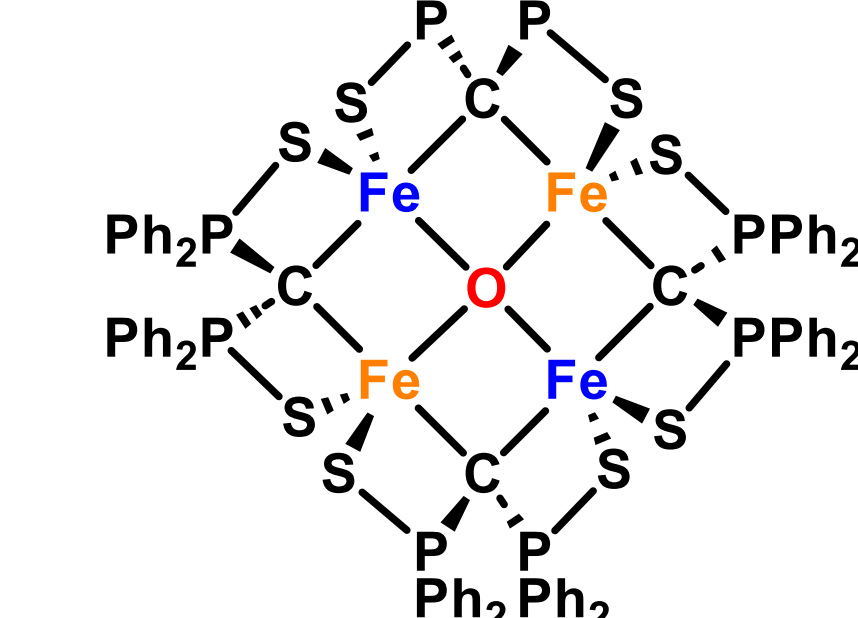
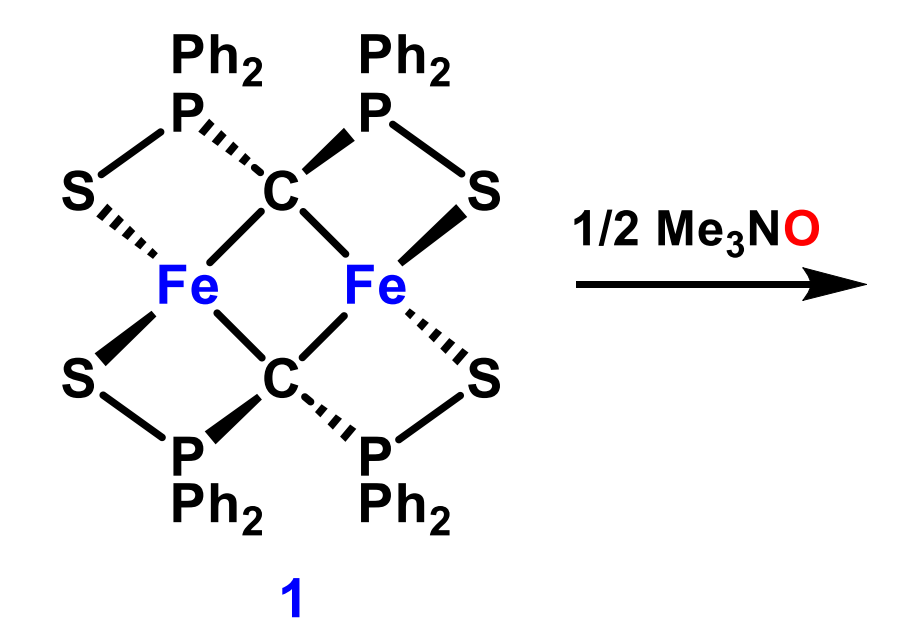
Bond	Fe(II)-Fe(II)	Fe(II)-Fe(III)
Fe(1)-C(1)	2.099(3)	2.0336(18)
Fe(1)-C(2)		2.0698(19)
Fe(1)-S(4)	2.380(1)	2.3109(5)
Fe(1)-S(1)		2.3171(6)
Fe(2)-C(1)	2.082(3)	2.0720(19)
Fe(2)-C(2)		2.0505(18)
Fe(2)-S(3)	2.355(1)	2.3409(6)
Fe(2)-S(2)		2.3479(6)
Fe(1)---Fe(2)	2.5680	2.5370

$Fe\cdots Fe$ (FeMo-Co) = 2.58 Å

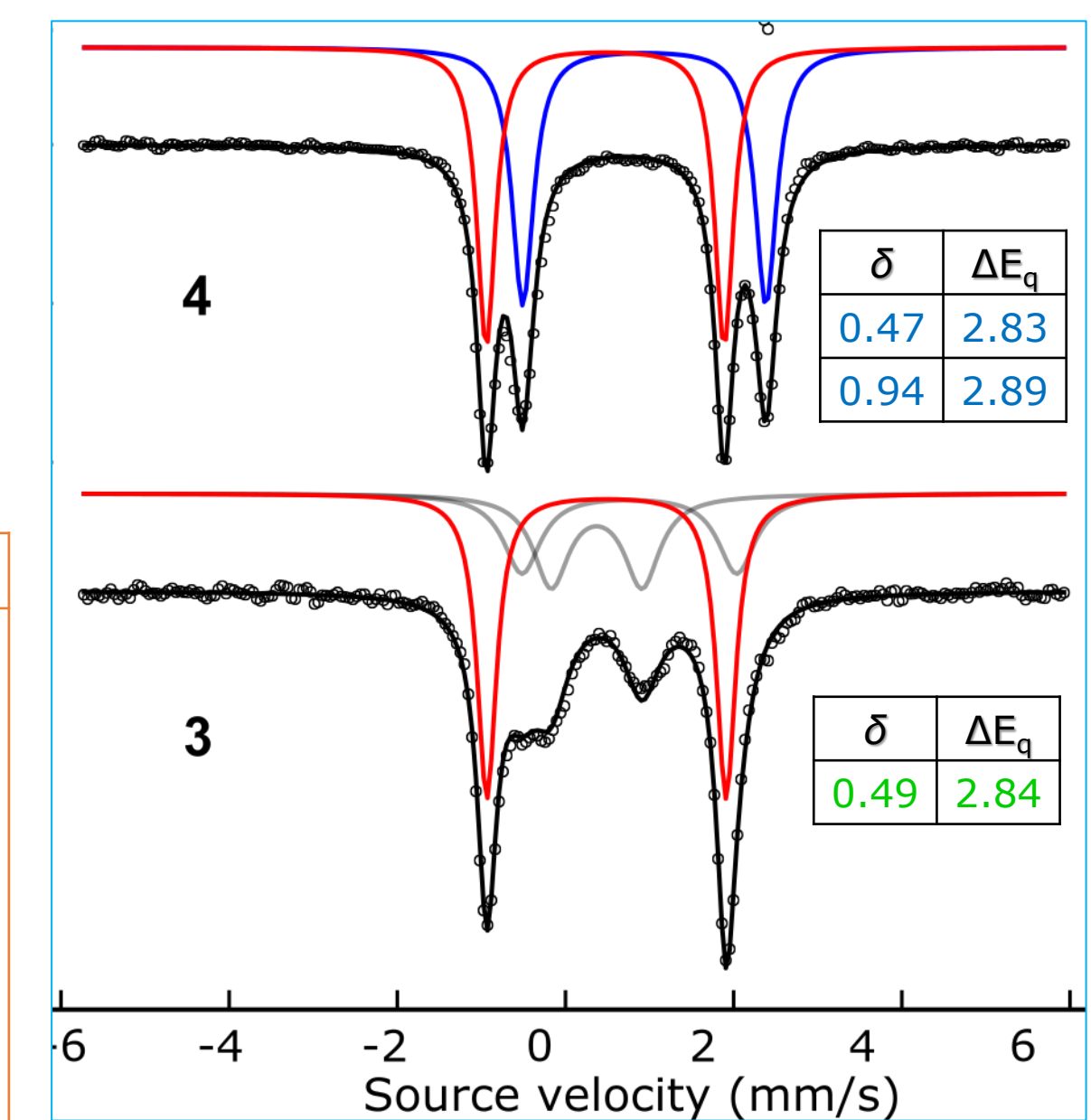
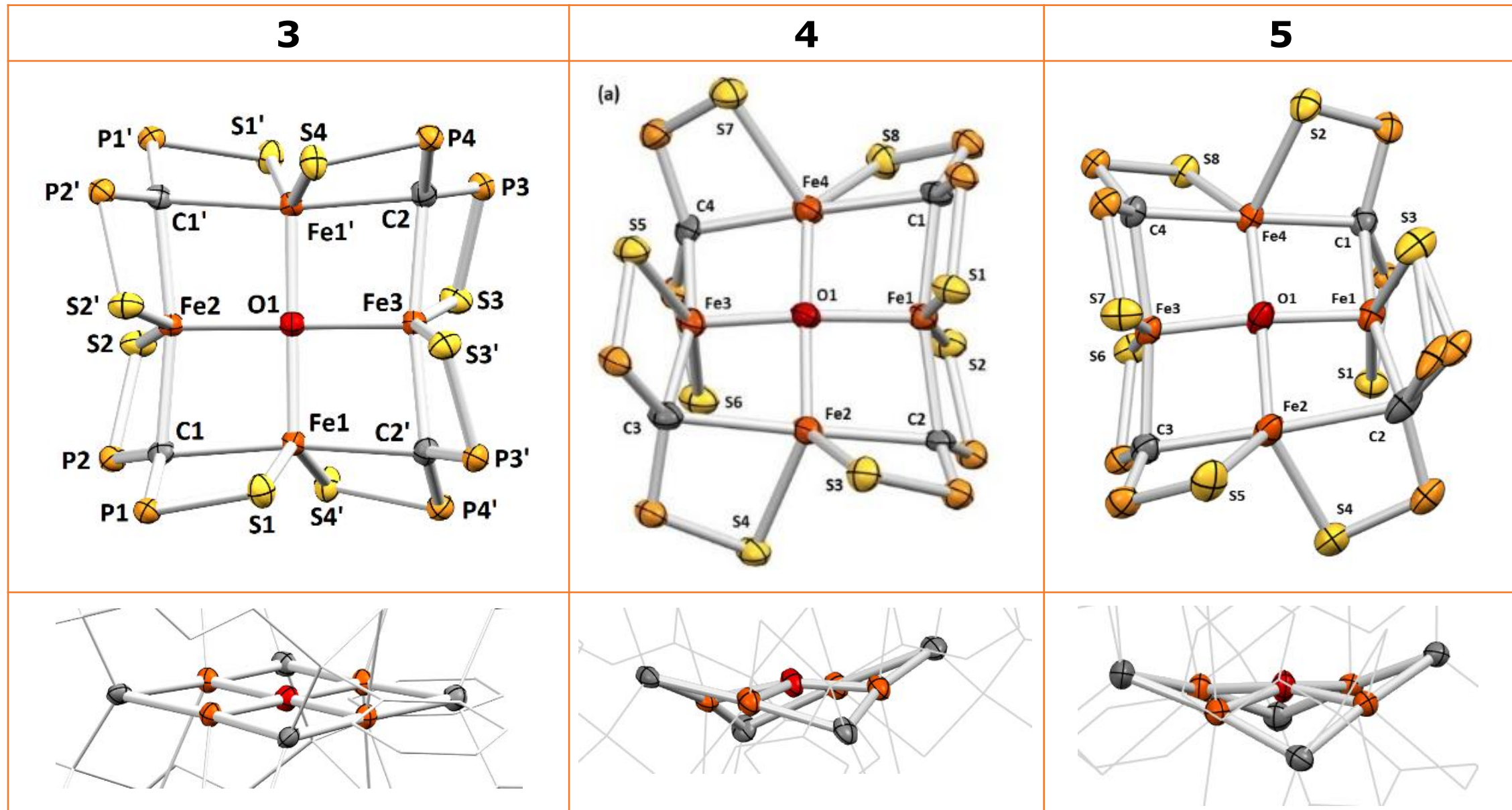
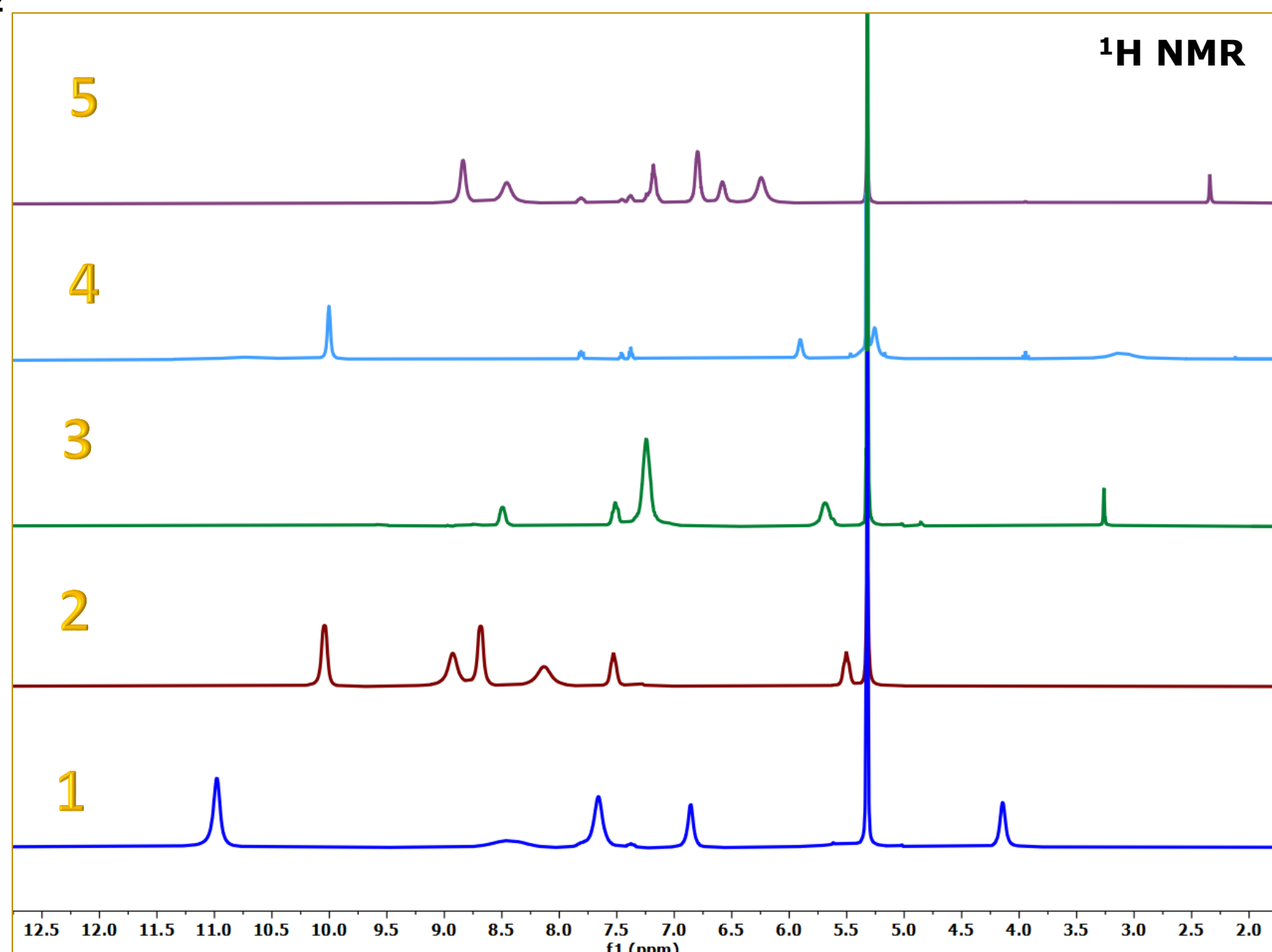
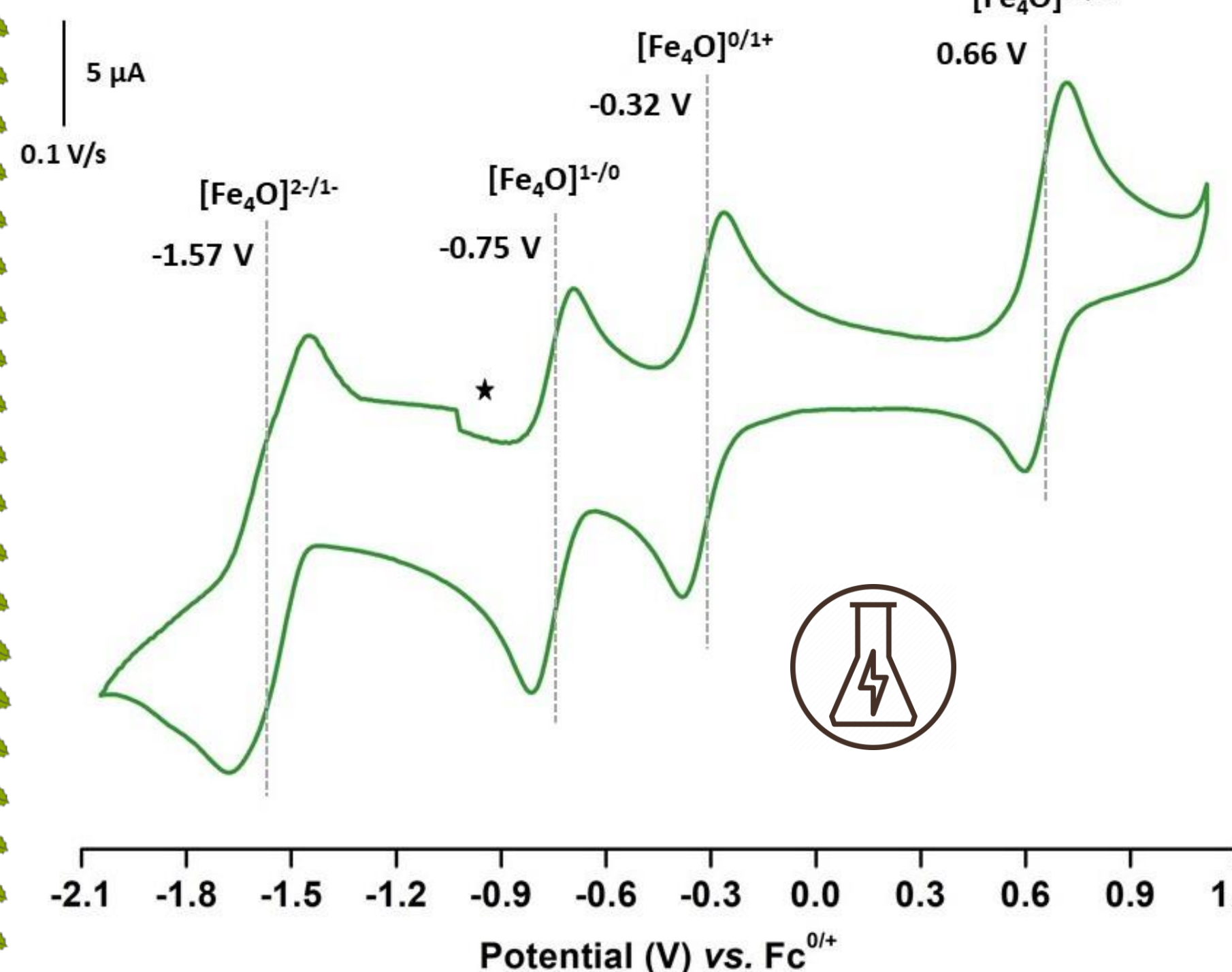
μ^4 -Oxo-Tetrairon Complexes



The $(SCS)^{2-}$ backbone being able to support one-electron oxidation, the next step was the chemical oxidation (with an oxygen atom donor), in the hope of building a complex of higher nuclearity by redox coupling.

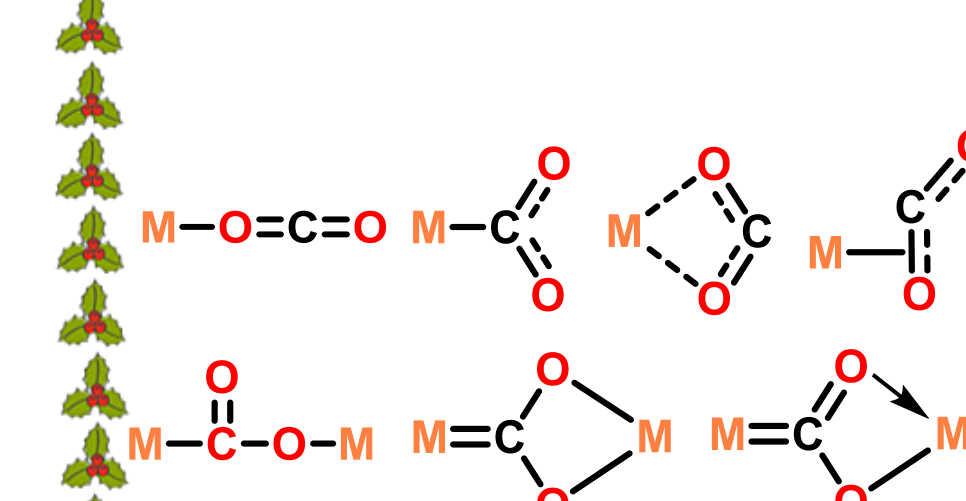


First ever oxo-bridged-Fe-Tetramer in variable redox state supported by organometallic backbone.

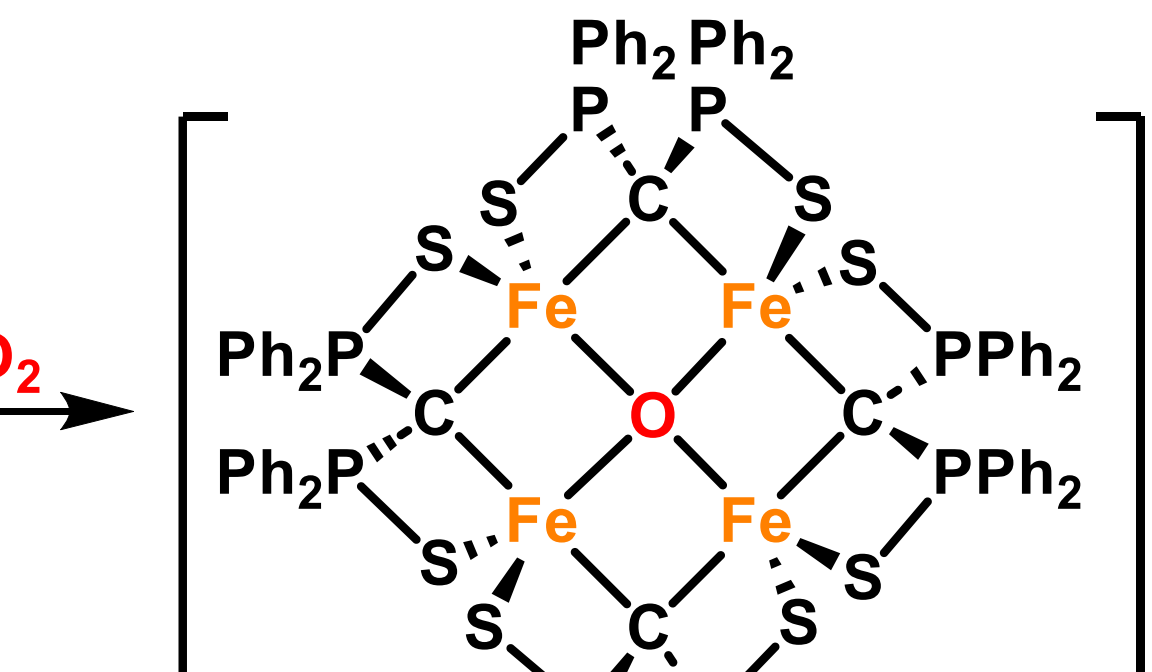
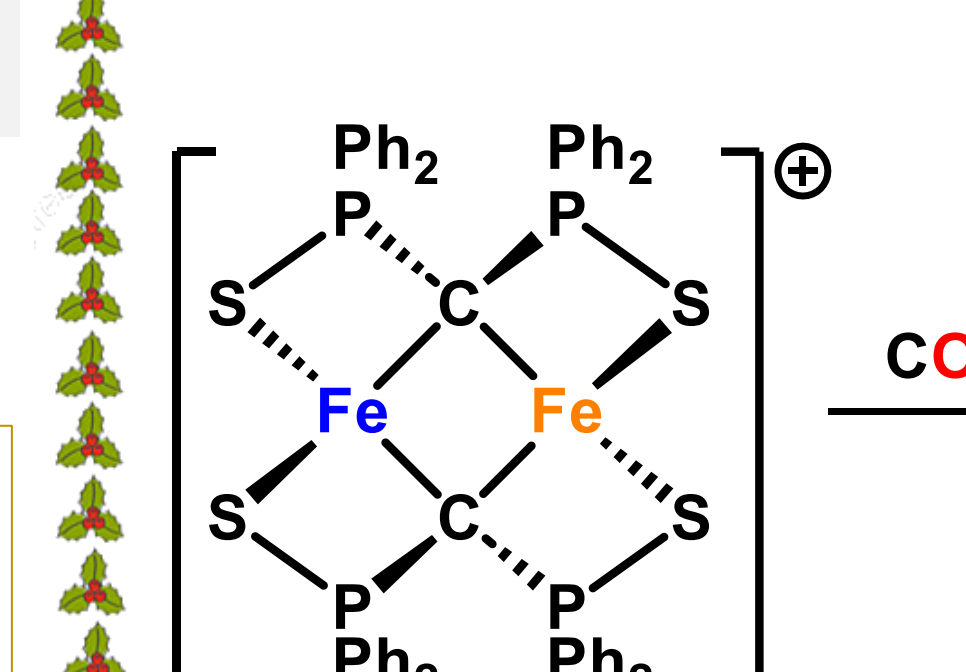


Bond	3	5	4
Fe-O _{avg}	1.9492	1.9715	1.9880
Fe-C _{avg}	2.1127	2.1589	2.1956
Fe-S _{avg}	2.3318	2.3690	2.4054
Fe---Fe	2.7585	2.7720	2.7940

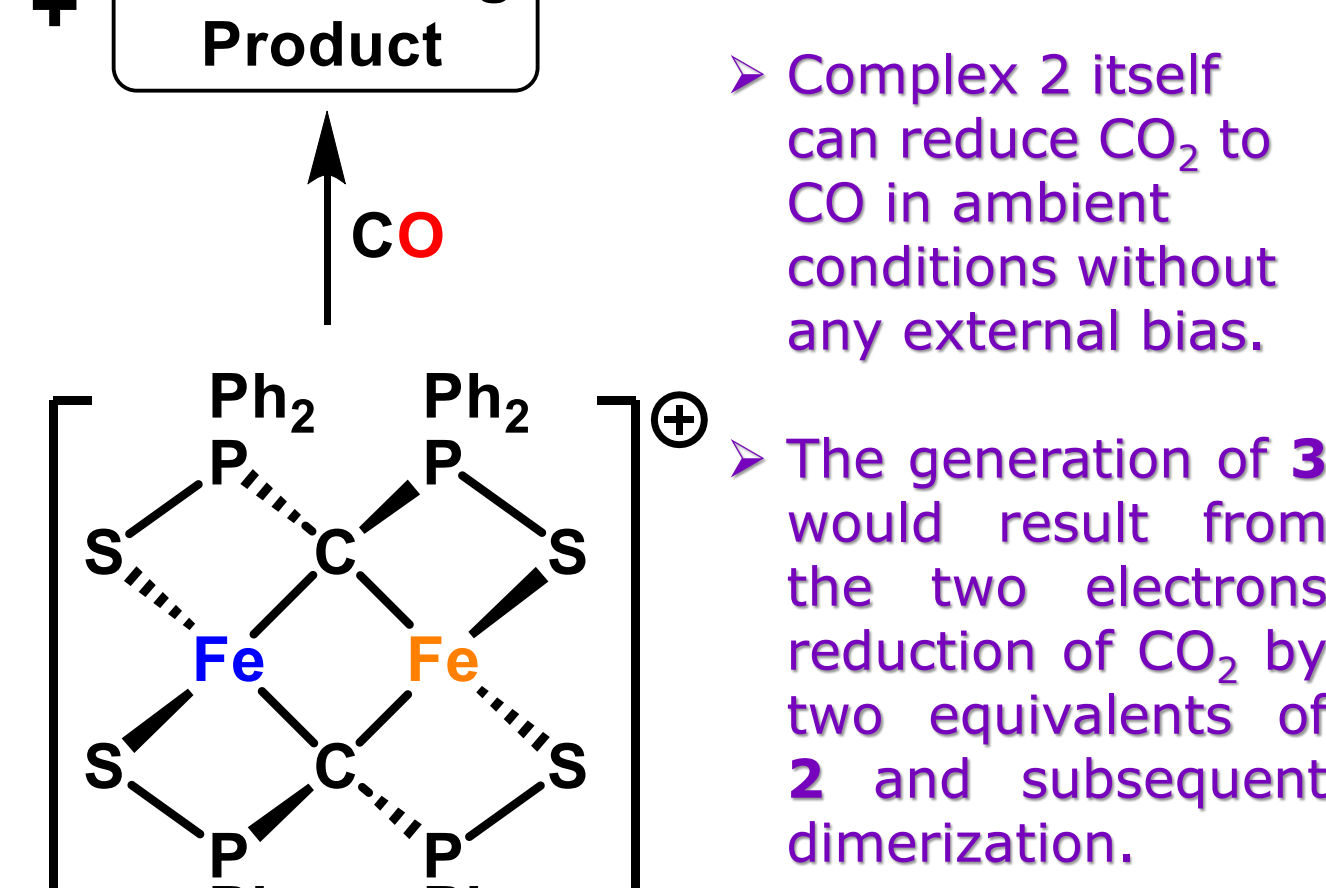
CO_2 Reduction



Depending upon the metal coordination and/ or the number of protons and electrons, the CO_2 can be transformed into its reduced analogue (CO , $HCOOH$, CH_4) or sometimes in the C-C coupling (oxalate, C_2H_4) product.



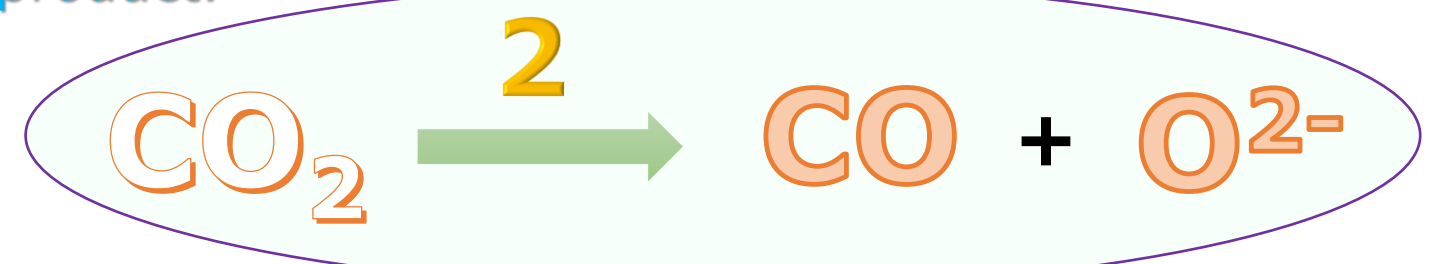
Molecular reduction of CO_2 by Fe(II/III) complex is yet unknown without going to a lower oxidation state (electro-chemically).



➤ Complex 2 itself can reduce CO_2 to CO in ambient conditions without any external bias.

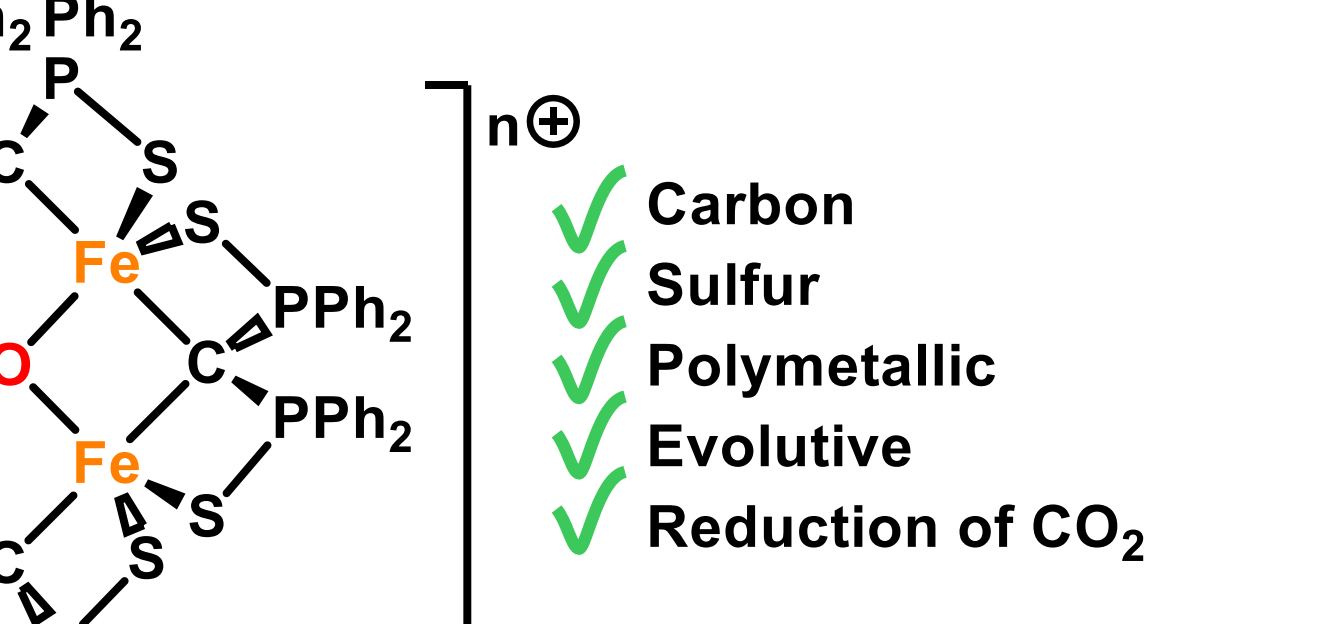
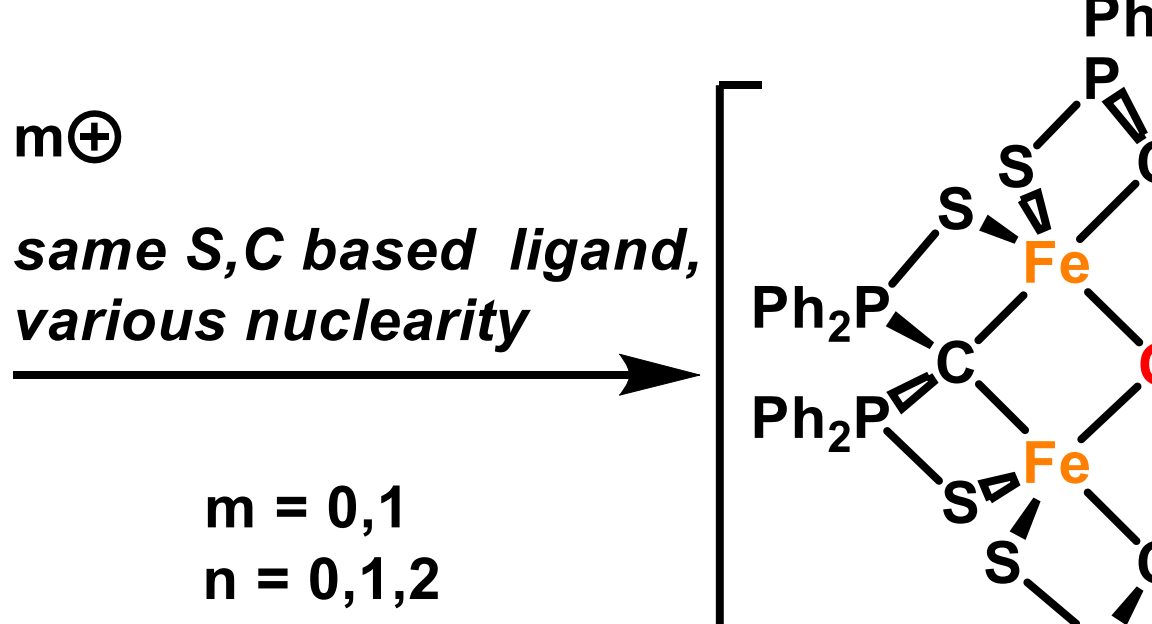
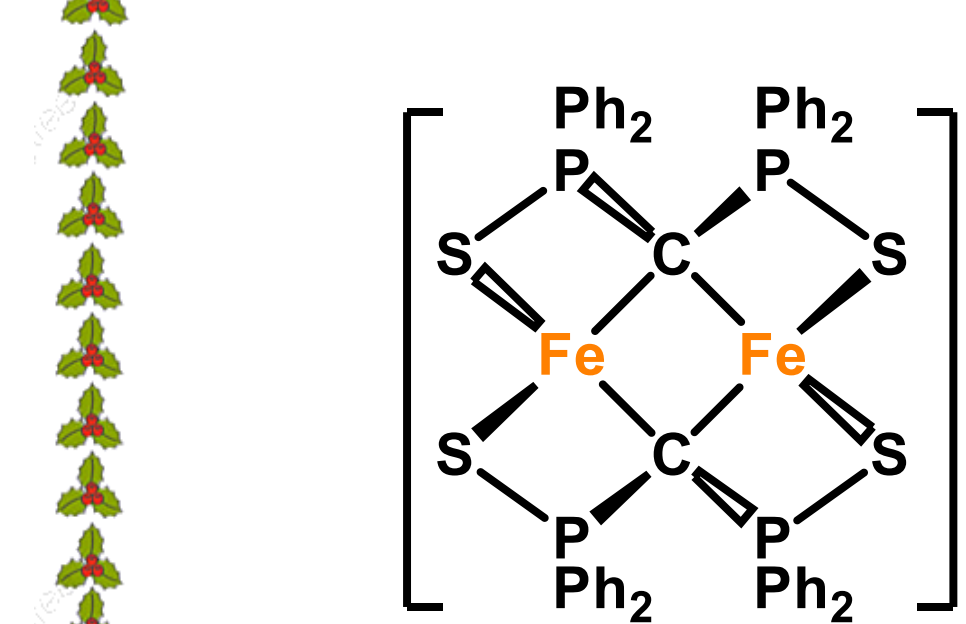
➤ The generation of 3 would result from the two electrons reduction of CO_2 by two equivalents of 2 and subsequent dimerization.

- ✦ The Greenhouse gas ' CO_2 ' can be transformed into CO & O^{2-} .
- ✦ CO can act as a primary building block for value-added chemicals.
- ✦ Oxide can be used as the soft oxidizing agent for substrate oxidation.



The oxide, generated *insitu*, can oxidize PPh_3 to $OPPh_3$ by oxo atom transfer (OAT)

Conclusion



Biomimetic redox-active Fe-Cluster similar to nitrogen reduction enzymes

CO_2 reduction catalysts with low-cost earth-abundant iron complexes

- ✓ Cleaner atmosphere by reducing greenhouse gas
- ✓ Atmospheric CO_2 as an oxidizing agent
- ✓ Renewable fuel catalysts by CO production

Increasing the knowledge on CO_2 recycling and artificial photosynthesis to achieve UN SDG 7 goals

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