Supporting Information for

Determinant role of the electrogenerated reactive nucleophilic species on the selectivity during the reduction of CO_2 catalyzed by Metalloporphyrins.

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	$M(P)^n$	$M(P)^{n-1}$	M(COOH)(P)	M(OCHO)(P)	M(H)(P)	M(PH)
Fe	3*	2	2	4*	2	2 / 4*[a] (degenerated)
Co	2	1	1	1	1	1
Rh	2	1	1	1	1	1
Ni	1	2	2	2	2	2
Cu	2	1	3*	3*	3*	3*
Zn	1	2	2	2	2	2
Pd	1	2	2	2	2	2
Ag	2	1	3*	1	3*	1
Cd	1	2	2	2	2	2
Ga	1	2	2	2	2	2
In	1	2	2	2	2	2
Sn	1	2	2	2	2	2
Sn(OH)	1	2	-	-	-	2

Table S1. Multiplicity of the ground state computed. The values with asterisk indicate that the ground state computed is not the lowest spin state. For complexes with transition-metals and Zn and Cd, the initial catalyst is the neutral complex, for complexes with p-metals Ga, In and the hydroxo-bonded Sn it is the cationic complex $[M(P)]^+$, and for the complex with Sn it is the dicationic complex $[M(P)]^{2+}$. The other intermediates are formed following a PCET step and thus with the same charge. [a] The doublet is presented in the manuscript.
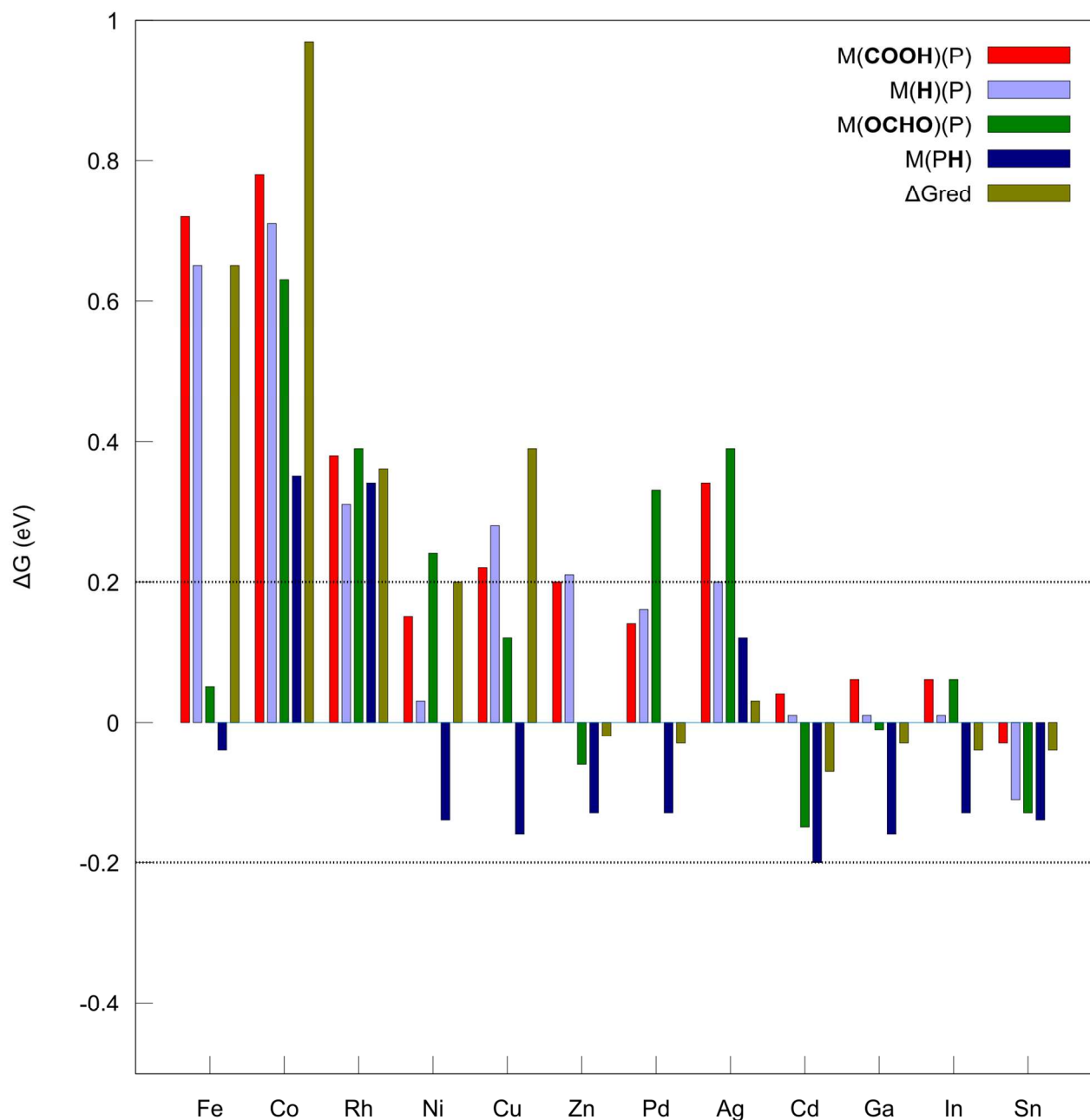
Figure S1. Free energy differences between the formation energies computed with PBE and PBE0 ($\Delta G_{CPET}(PBE0) - \Delta G_{CPET}(PBE)$). For the calculation of ΔG_{CPET} with PBE0, the free energies of the individual species are obtained by the sum of the SCF energies computed with PBE0 by a single point calculation on the geometries optimized with PBE, and of the finite temperature corrections calculated with PBE.
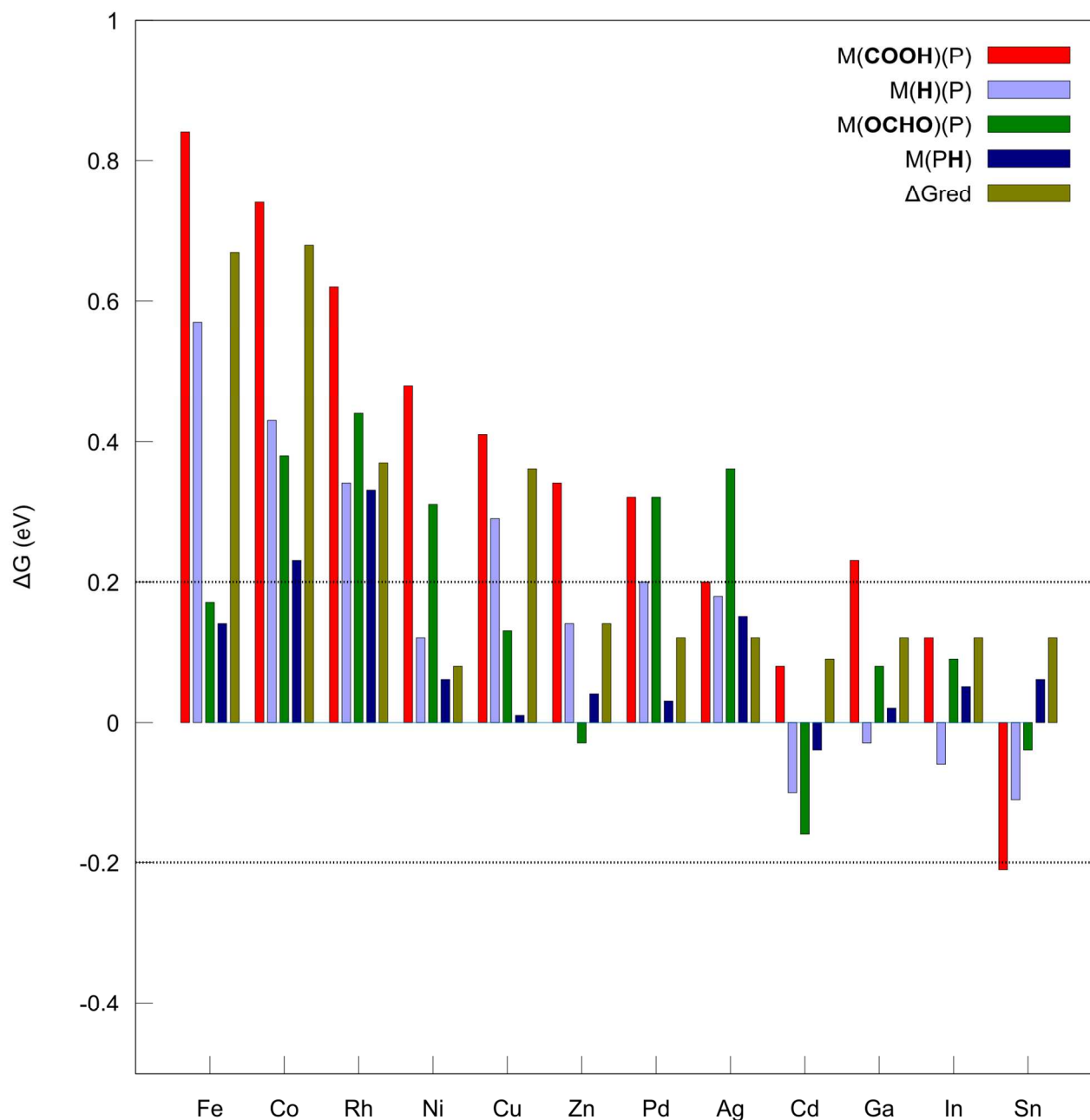
Figure S2. Free energy differences between the formation energies computed with PBE and B3LYP (ΔG_{CPET}(B3LYP) − ΔG_{CPET}(PBE)). For the calculation of ΔG_{CPET} with B3LYP, the free energies of the individual species are obtained by the sum of the SCF energies computed with B3LYP by a single point calculation on the geometries optimized with PBE, and of the finite temperature corrections calculated with PBE.

Computation of absolute reduction potentials

For the computation of the theoretical reduction potentials, we used the equation, $E_{red} = -\frac{G_{red} - G_{ox}}{nF}$, to compute absolute reduction potentials, where G is the free energy computed directly in solution with an implicit solvation model (the finite temperature corrections to the energy are computed in solution at T=298.15 K and assuming ideal gas at p=1 atm). This methodology is not fully rigorous as the free energies in solution should in principle be computed using thermodynamics cycles, which implies the computation of gas phase free energies and solvation energies. However, we believe that in our case it is sufficient as we don't aim at quantitative predictions and furthermore, several studies reported that differences between free energies computed directly within the implicit solvation model give similar results to thermodynamic cycles.[1,2] The computed values are then referenced to the absolute potential of the standard hydrogen electrode, 4.44 eV (IUPAC recommended value).[3] As no experimental values were found for metalloporphine complexes, we reported values obtained for MP with substituted porphyrin ligands, TPPS: tetrakis(sulfonatophenyl)porphyrin and TPPC: tetrakis(*p*-carboxyphenyl)porphyrin obtained in water and protoporphyrin IX. The reduction potentials of TPPS and TPPC are close (ΔE < ~ 0.2 V) and reduction potential of TPPS is found to be very similar to TPP: tetraphenylporphyrin in aprotic solvent according from ref 4.[4] In turn, we expect the reduction potentials of metalloporphine complexes to be similar to the one of complexes with TPP ligand but probably shifted to more negative values due to the less extended π-system.

metal	DFT	Exp
Fe	-1.11	-1.30[a]
Co	-0.87	-1.10[a]
Rh	-0.17	
Ni	-1.23	(~ -1.5)[a]
Cu	-1.27	-1.05[b]
Zn	-1.43	-1.16[b] / -1.25[d]
Pd	-1.44	-1.04[b]
Ag	-1.04	-
Cd	-1.36	-1.05[b]
Ga	-1.06	~ -0.90[c]
In	-1.02	~ -0.80[c]
Sn(OH)	-0.87	-0.56[b] / -0.73[d]

Table S2. Theoretical reduction potentials in water (*vs* SHE) computed for the metalloporphine complexes (DFT) and experimental reduction potentials (*vs* NHE) for complexes with various porphyrin

ligands (exp). [a]: Immobilized protoporphyrin IX complex in DDAB film.[5] [b]: TPPS (Zn and Pd,[4] Cu, Cd and Sn[6]). [c]: Values obtained by adding -0.30 V to the half-wave potentials measured for TMPyP: tetrakis(N-methylpyridinium) ligand.[7] This shift is derived from ref 3 to deduce the approximate potential with the TPPC ligand for Ga and In. [d]: TPPC.[8] The values obtained are in correct agreement with the experimental potentials reported as the average discrepancy is ~ 0.22 (for Pd and Cd it is higher 0.4, 0.3 eV). However, as mentioned before there may be a systematic shift towards more negative values due to the presence of the substituent for the experimental potentials.

	$[M(CO_2)]P]^{n-1}$	$[M(OCO)]P]^{n-1}$
Fe	0.33	dissociation
Co	0.30	dissociation
Rh	0.02	dissociation
Ni	0.62	dissociation
Cu	dissociation	dissociation
Zn	0.98	dissociation
Pd	dissociation	dissociation
Ag	dissociation	dissociation
Cd	0.61	0.46
Ga	0.68	0.42
In	0.59	0.38
Sn(OH)	-*	-*

Table S3. Thermodynamics (in eV) for the association between CO_2 and the reduced catalyst with the formation of the CO_2 adducts $[M(CO_2)P]^{n-1}$ (metal-carbon bond) and $[M(OCO)P]^{n-1}$ (metal-oxygen bond). n=0 for Fe, Co, Rh, Ni, Cu, Zn, Pd, Ag, Cd, and +1 for Ga, In and Sn(OH). * The presence of the hydroxo ligand prevents the formation of the CO_2 adduct.

References

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