The Abdus Salam International Centre for Theoretical Physics

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2269-2

Workshop on New Materials for Renewable Energy

17 - 21 October 2011

Quantum chemcial characterization of homogeneous catalytic processes for water splitting and Co2 reduction

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CHEMISTRY

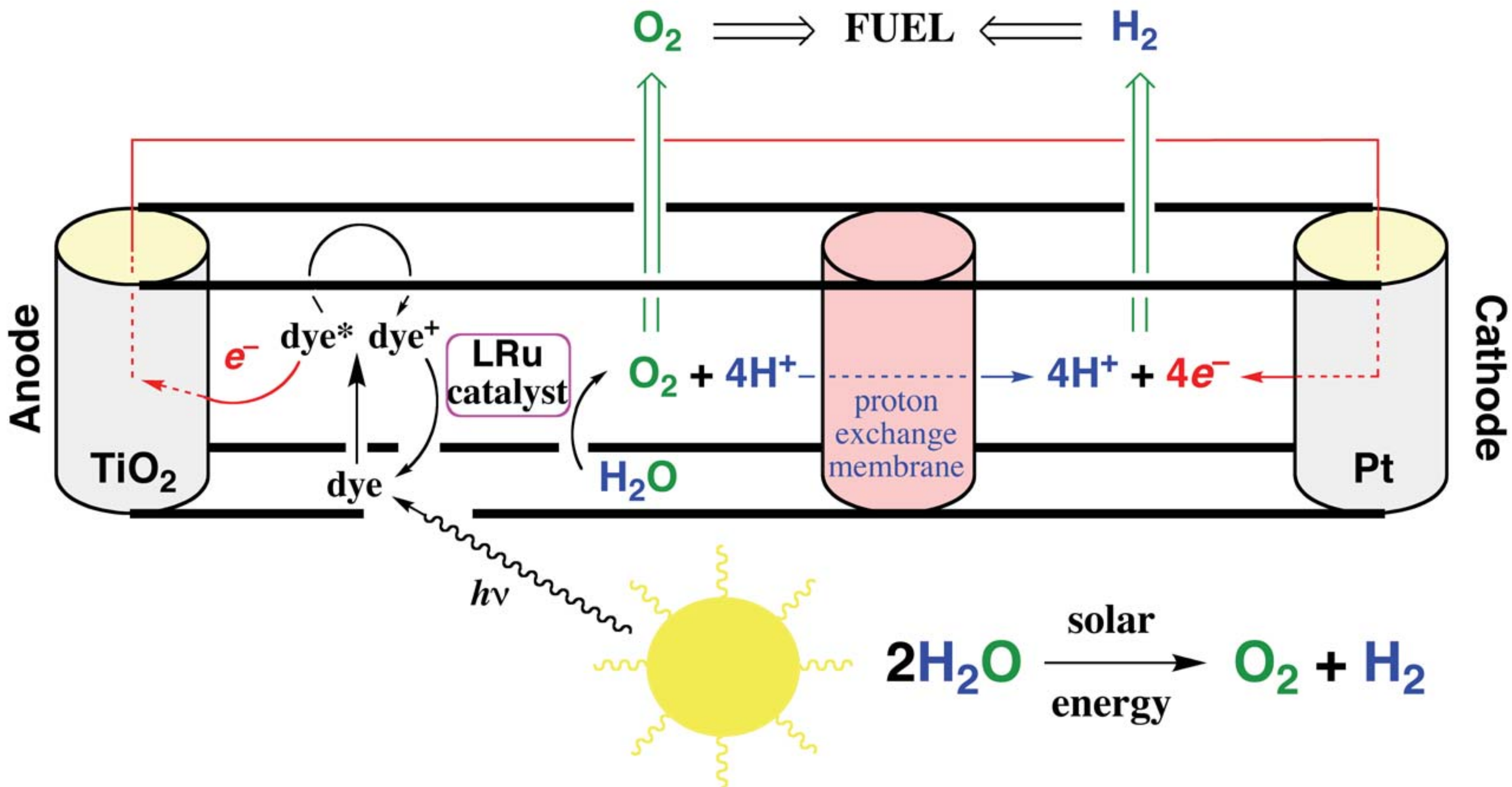
Quantum Chemical Characterization of Homogeneous Catalytic Processes for Water Splitting and CO_2 Reduction

Christopher J. Cramer

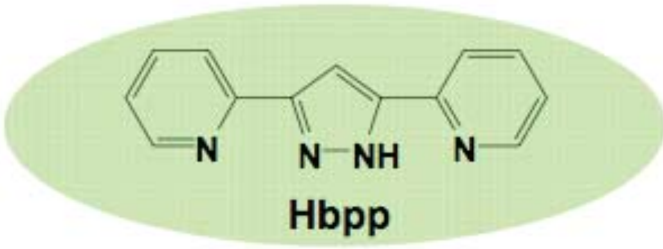
Trieste, October 19, 2011

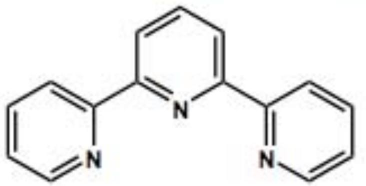
Conversion of Solar Energy to Green Fuel

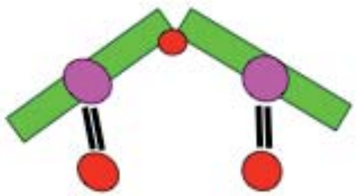
Schematic of the Dye-Sensitized Solar Cell



Ru FUNCTIONAL MODELS: Ru-HBPP

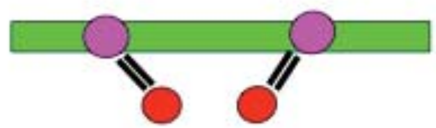






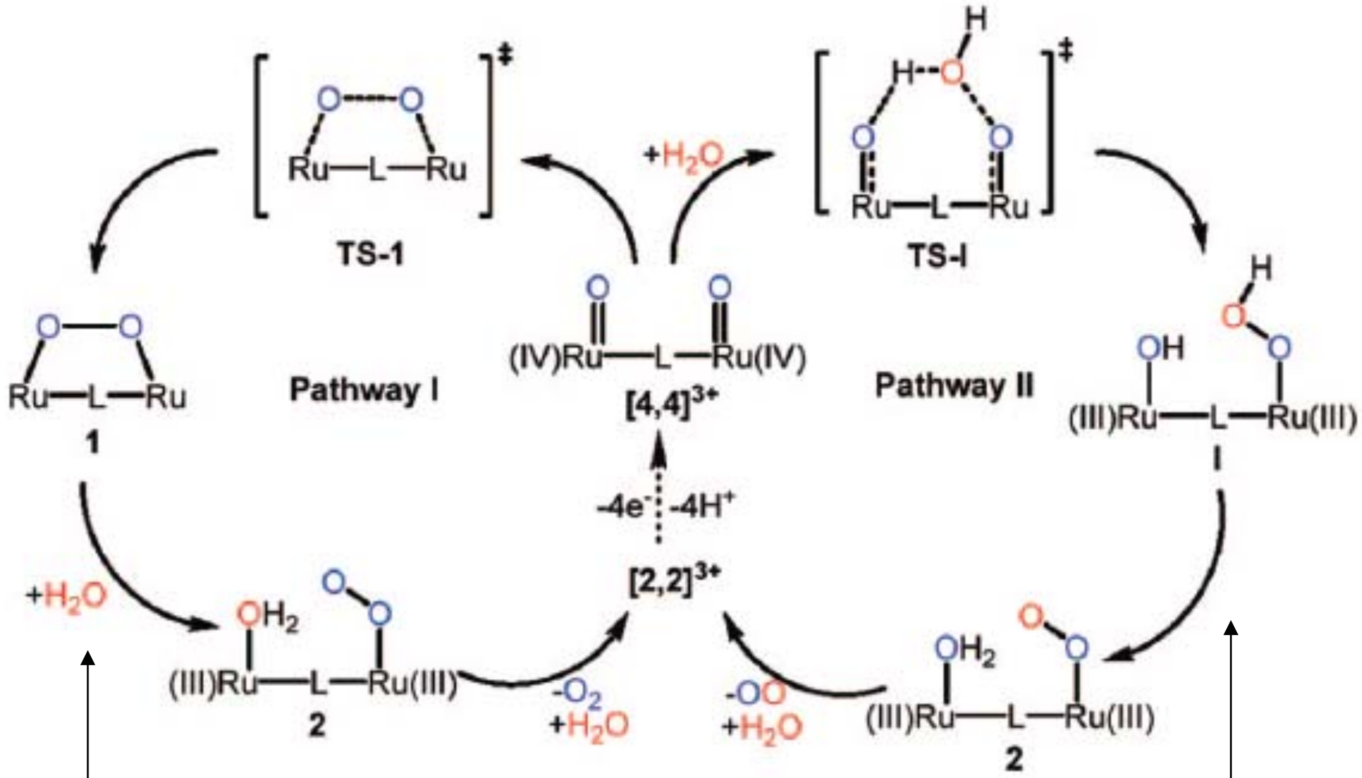
$[(trpy)Ru^{II}\text{-}(bpp)\text{-}Ru^{II}(trpy)]^{3+}$

H_2O OH_2



Sens, C.; Romero, I.; Rodríguez, M.; Llobet, A. et al., *J. Am. Chem. Soc.*, **2004,** *126*, 7798
Sala, X.; Romero, I.; Rodriguez, M.; Escriche, L.; Llobet, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 2842

Mechanism of Water Oxidation Catalysis

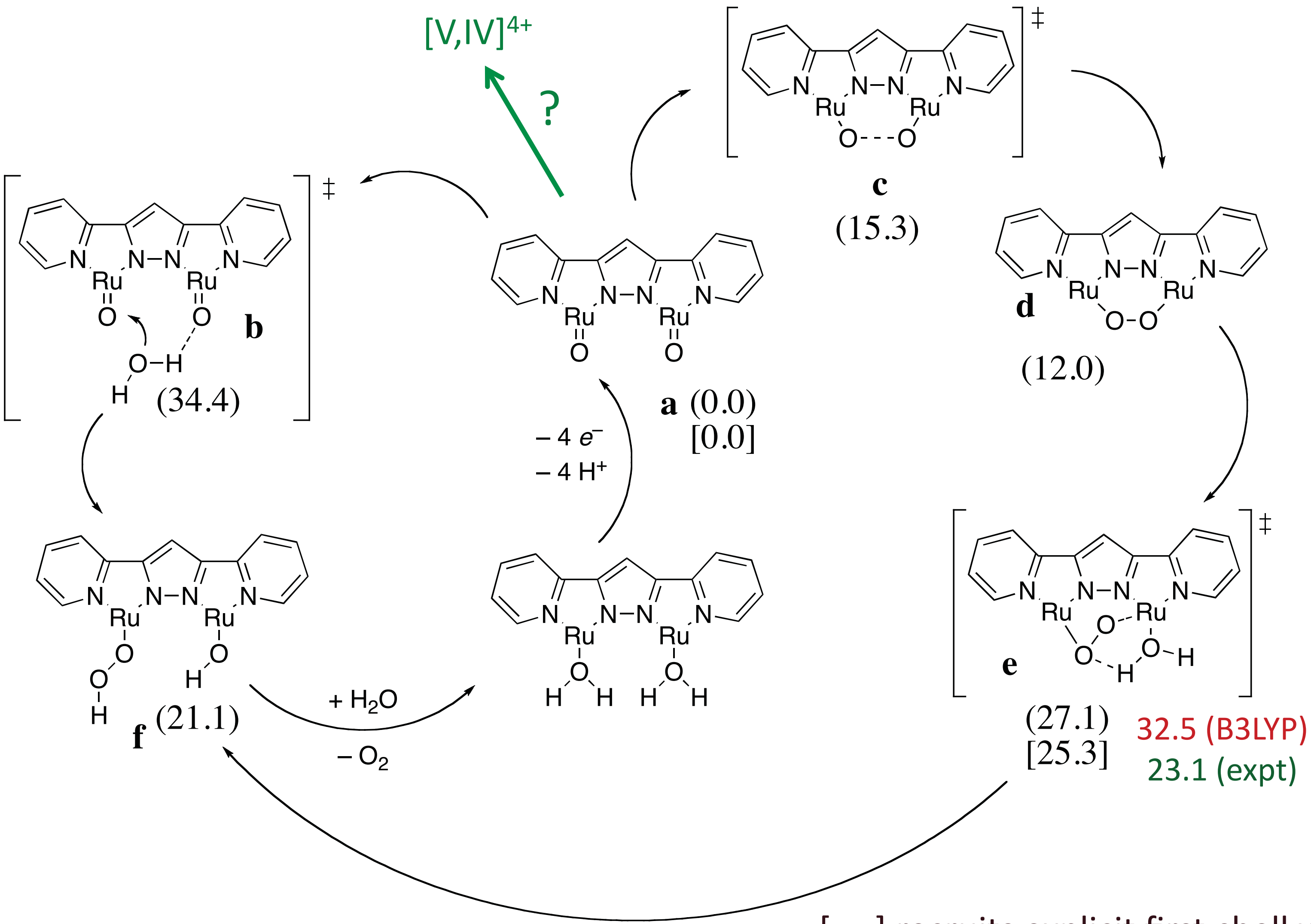


Activation enthalpy too high to be mechanistically viable (predict 32.5 kcal/mol, expt measured as 23.1 kcal/mol)

Proposed pathway <u>following protonation of activated catalyst</u>

PCM/B3LYP: Yang and Baik, *JACS* **2008**, *130*, 16231

Catalytic Cycle Energies (kcal/mol)

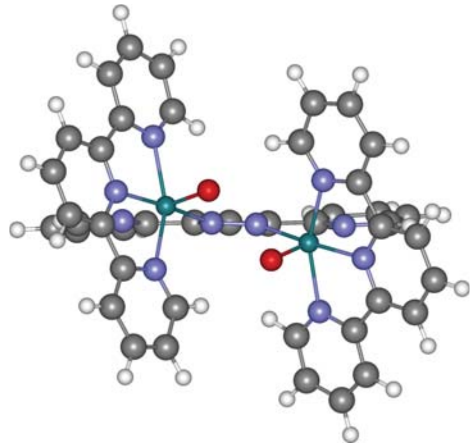


[…] recruits explicit first-shell water

SMD/M06-L/large basis

The electronic structure of $[4,4]^{3+}$

1. Ground state?
2. $Ru^{III}–O^{-•}$ spins locally coupled triplet

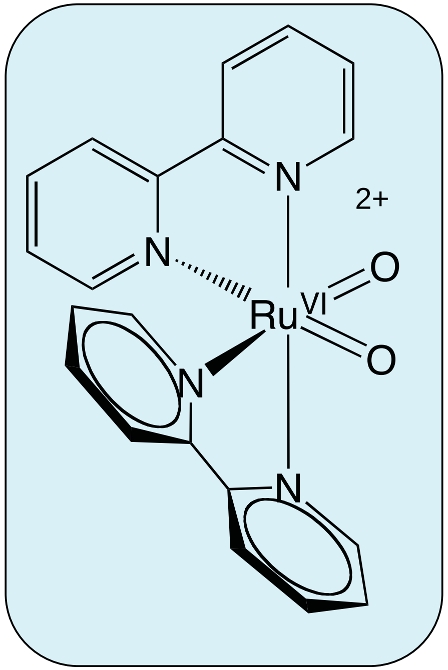


	Q	S_0 (AF)	S_1 (CS)	T
CASSCF	-0.8	0	26.5	-0.8/13.5
CASPT2	0.5	0	32.5	0.7/16.6
DFT/B3LYP	-0.8	0	44.8	7.2
DFT/M06L	-1.0	0		9.3

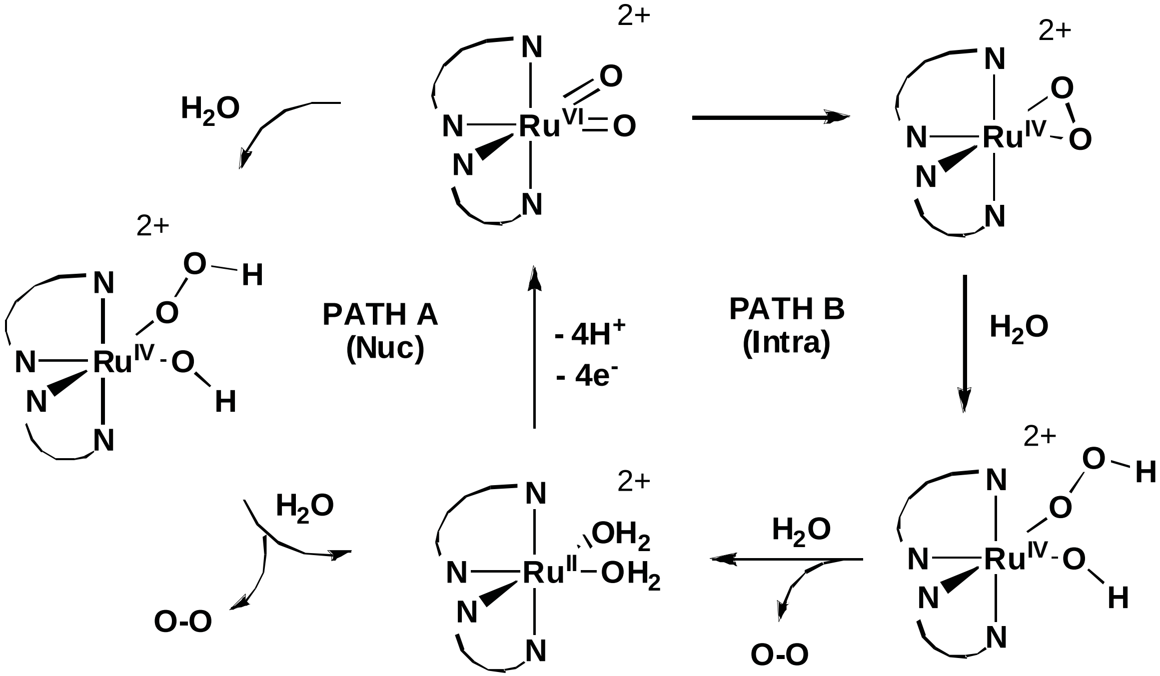
Q: 82 % weight
S_0: 15 % AF + mixture of 4 different closed-shell config. (15 % weight each)
S_1: 43 % CS + 11 % AF + some other CS config. with ~5 % weight each
T: two degenerate + 1 lower in energy: strongly multireference character

O–O bond formation facilitated by spin coupling

A Mononuclear Case

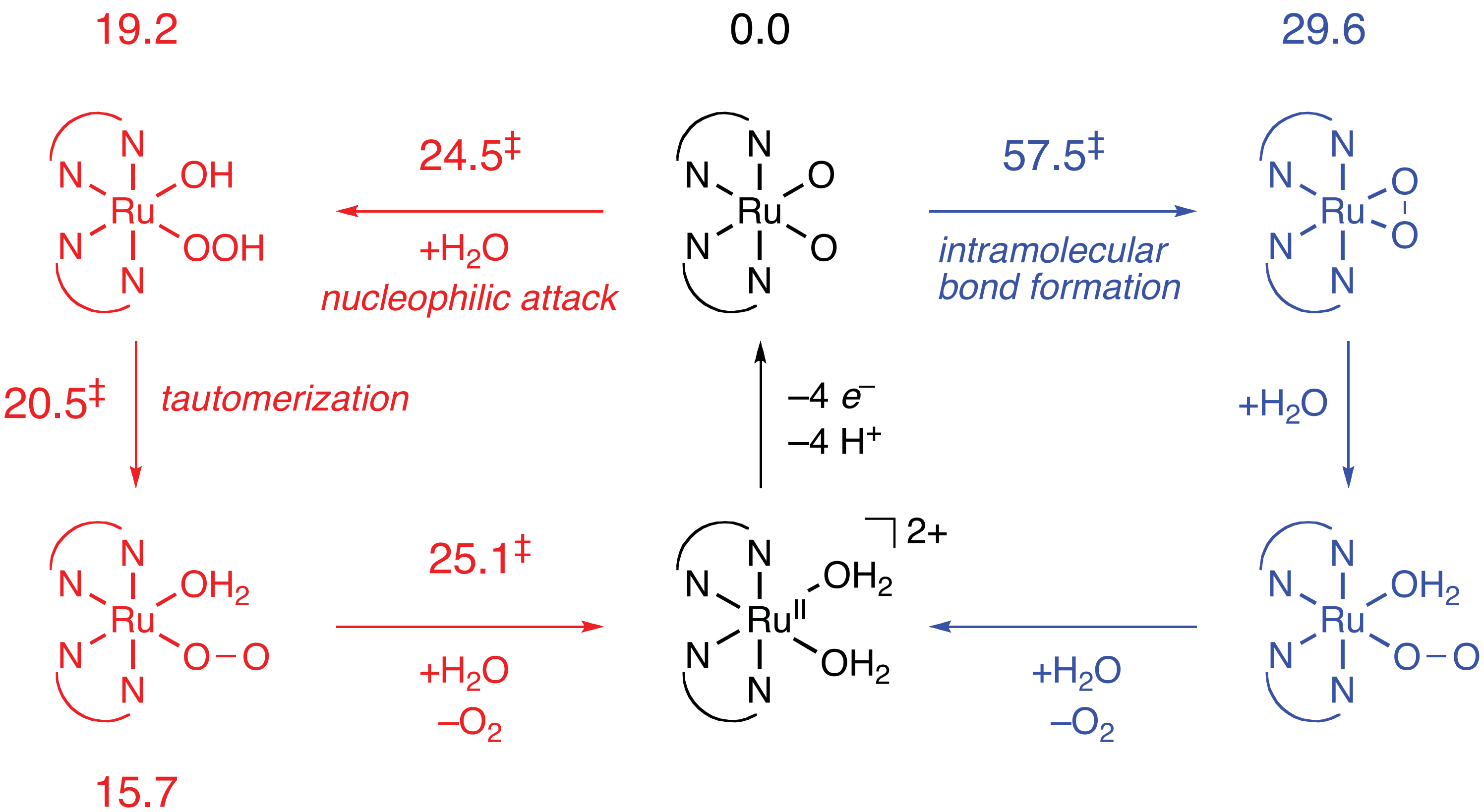


Collin and Sauvage *IC* **1986**, *25*, 135
Dobson and Meyer *IC* **1988**, *27*, 3283

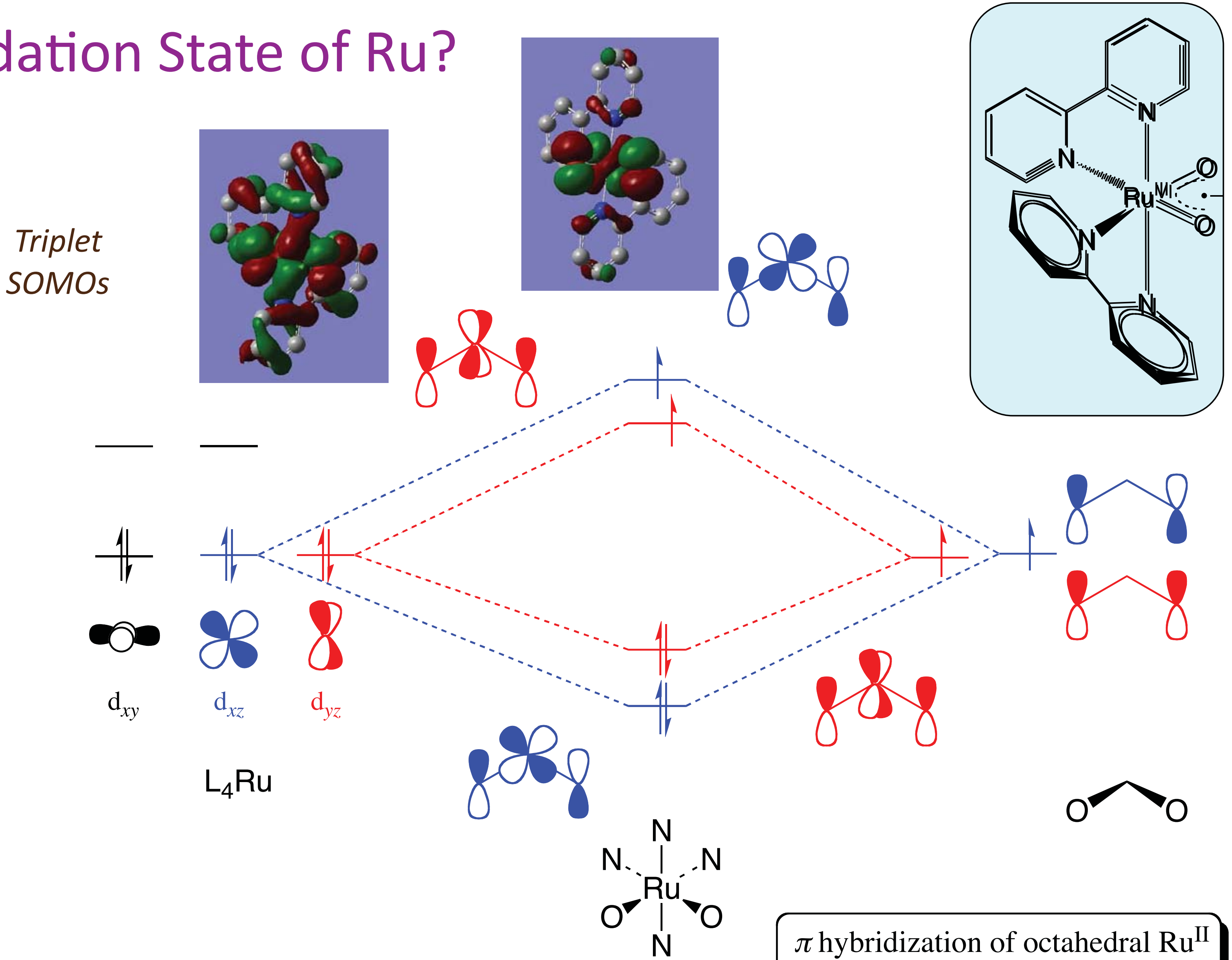


Not originally recognized as a water splitting catalyst owing to decomposition in situ to RuO_2
– Llobet et al. identify O_2 *evolution from oxidation of* cis *aquo – mechanism?*

Mechanistic Quantification (kcal/mol)



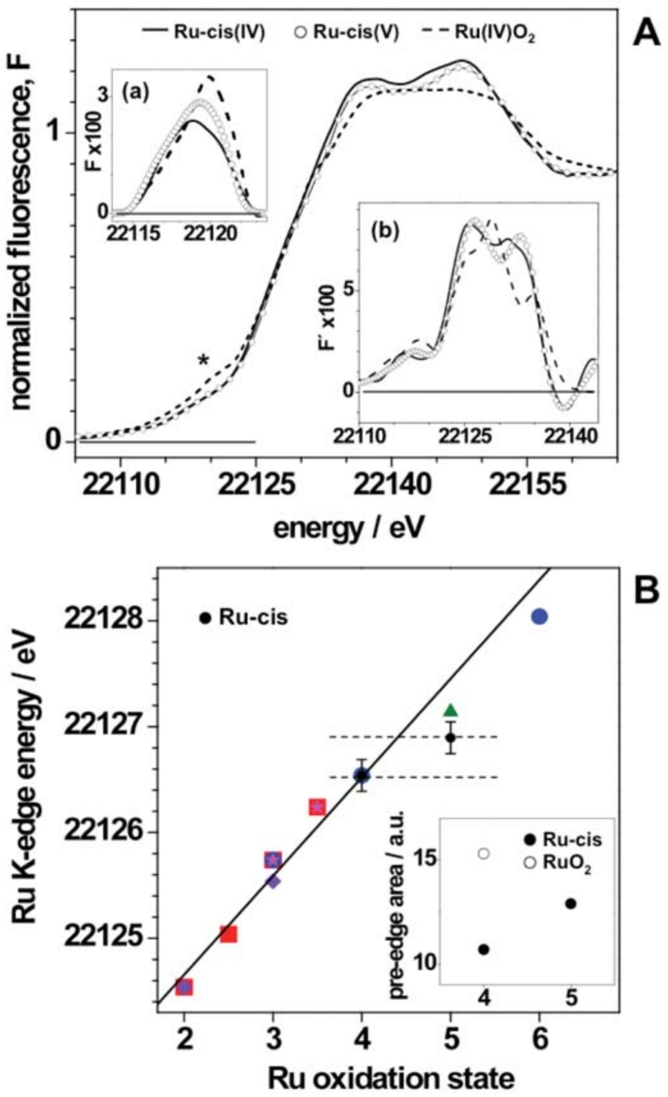
Oxidation State of Ru?

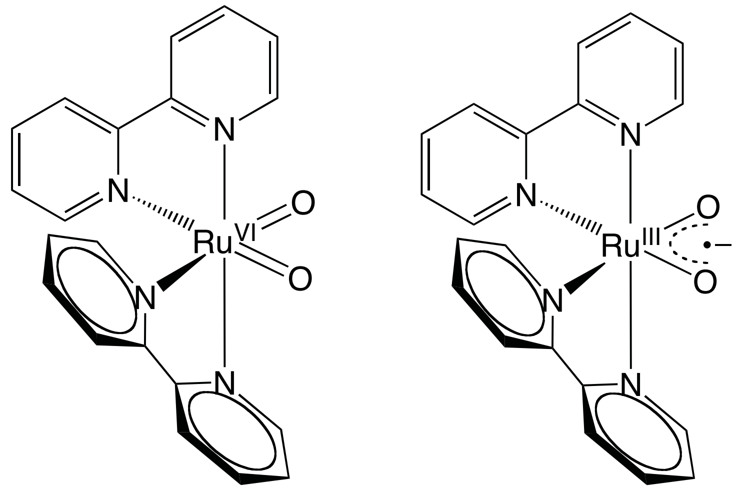


π hybridization of octahedral Ru^{II}
d orbitals with 2 neutral O atoms

Sala et al. *Angew. Chem. Int. Ed.* **2010**, *49*, 7745.

Oxidation State of Ru?





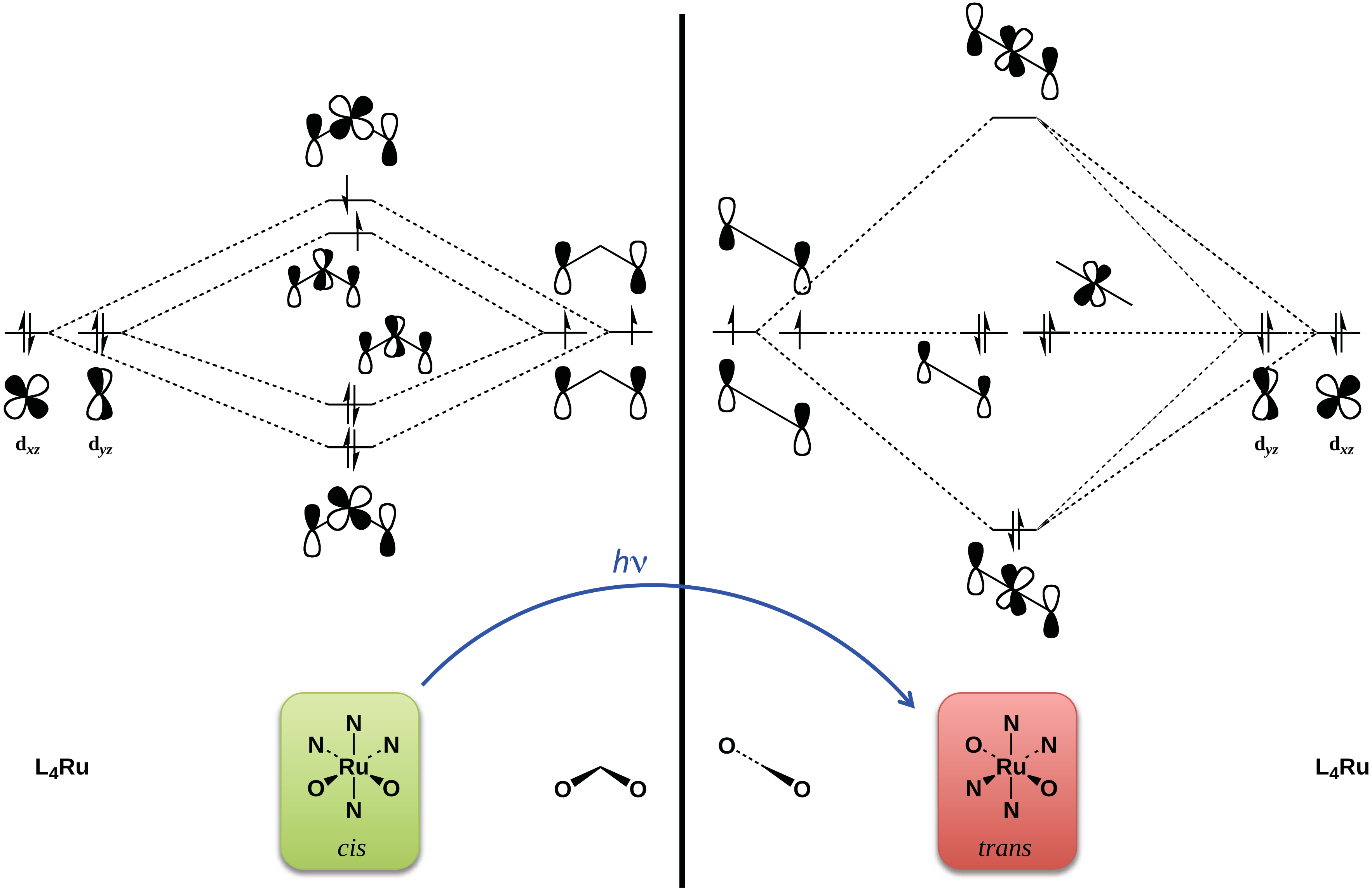
Note that XAS figure presupposes its own conclusion, by pinning data points to formal oxidation numbers…

4 = dihydroxo
5 = hydroxo/oxo

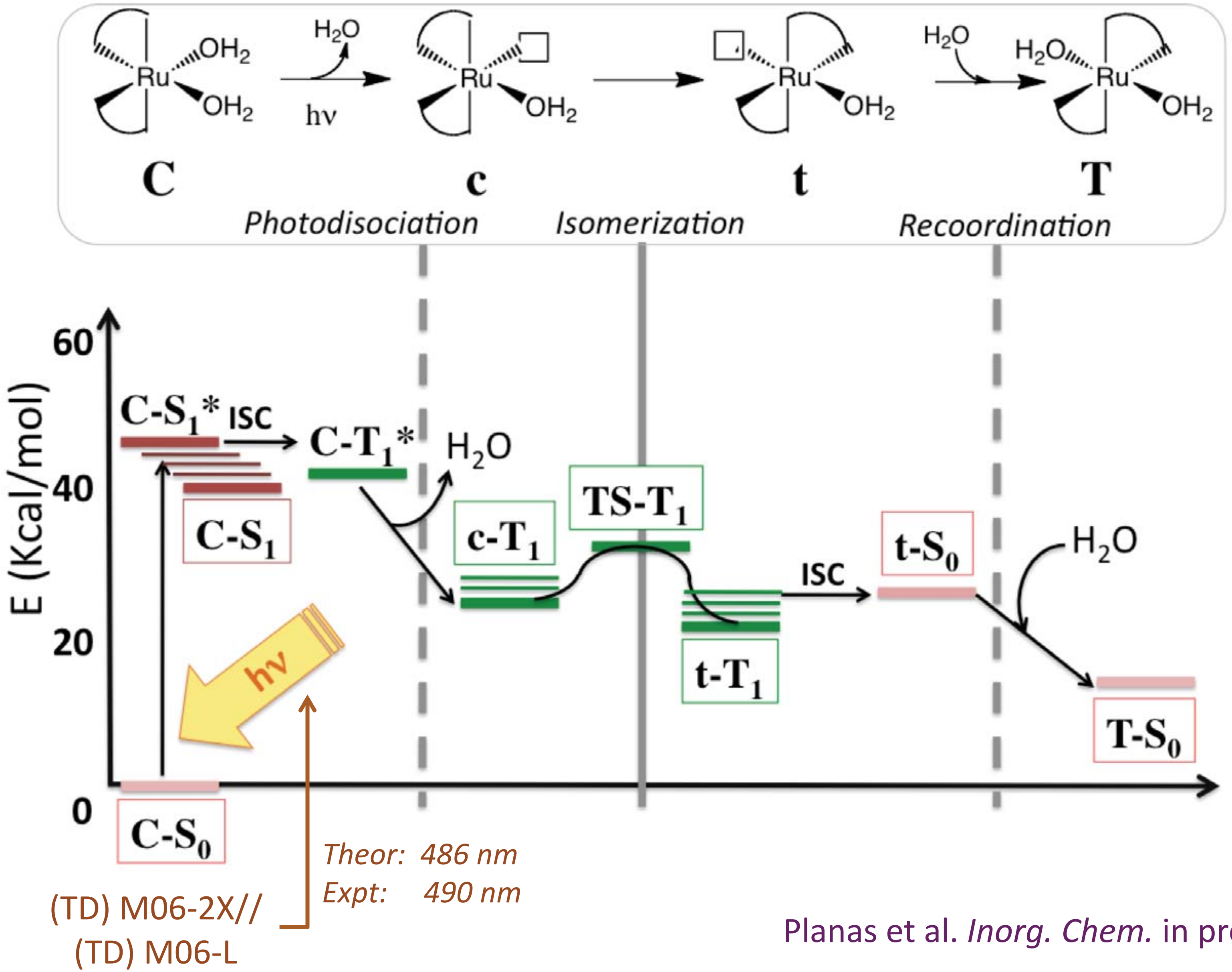
Planas et al. *Inorg Chem.* in press.

Unreactive *trans* Species Generated from Photoisomerization

3.8 S-T splitting (kcal/mol) 34.7



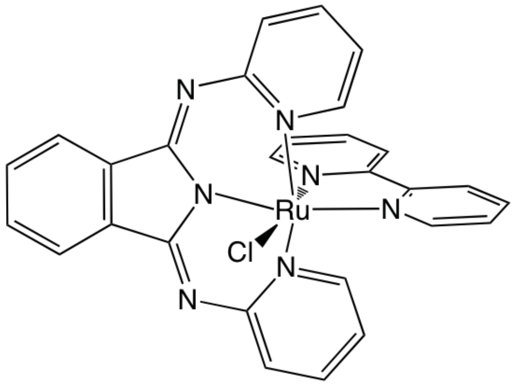
Unreactive *trans* Species Generated from Photoisomerization

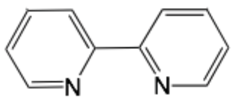


Planas et al. *Inorg. Chem.* in press.

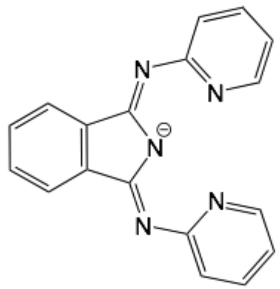
Something Besides Water Splitting

Hydrogenative CO_2 Reduction



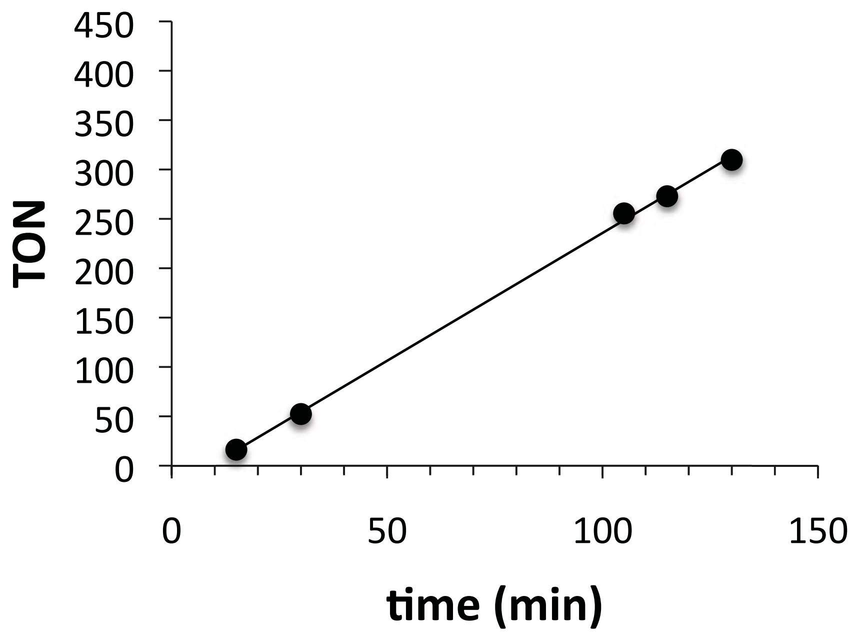


bpy

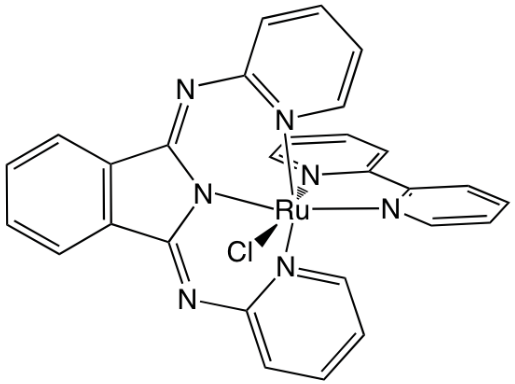


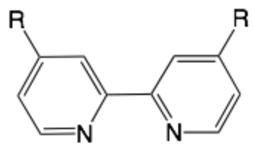
bid-

Catalytic Experiments

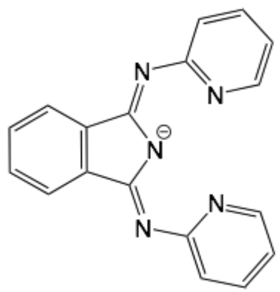


Hydrogenative CO_2 Reduction





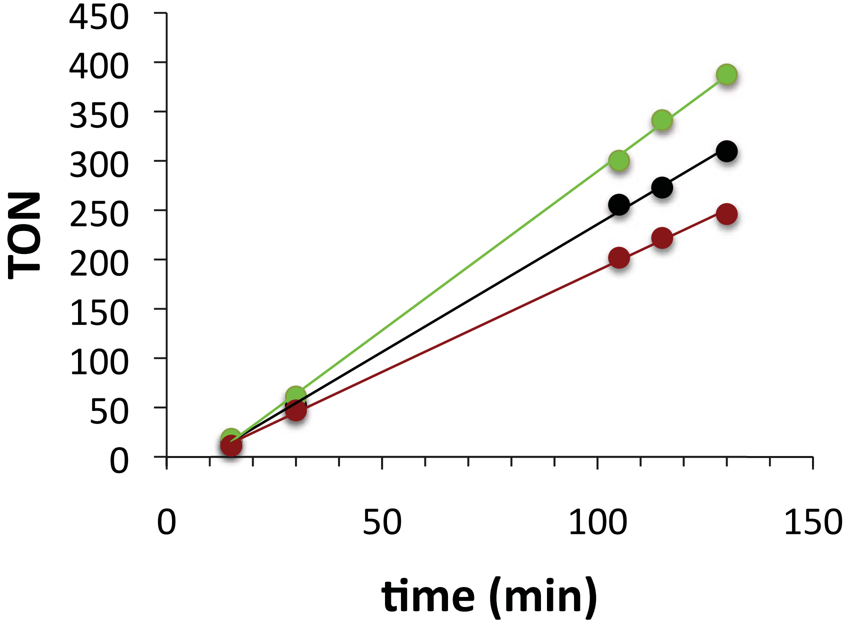
bpy



bid-

R = -COOEt or -OMe

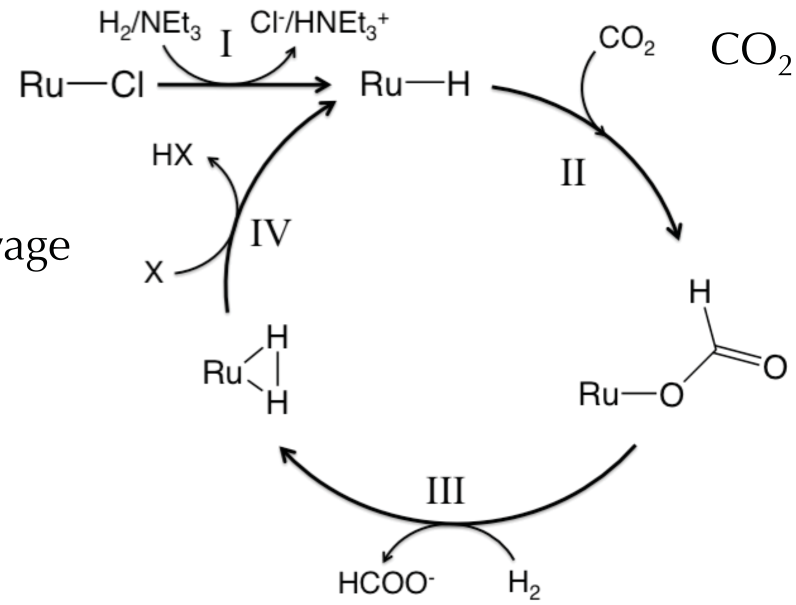
Catalytic Experiments



Hydrogenative CO_2 Reduction

Proposed Catalytic Cycle

CO_2 insertion



Heterolytic Cleavage

Ligand Substitution

Computational Details

Density Functional Theory (Gaussian09)

M06-L Functional (Meta-GGA)

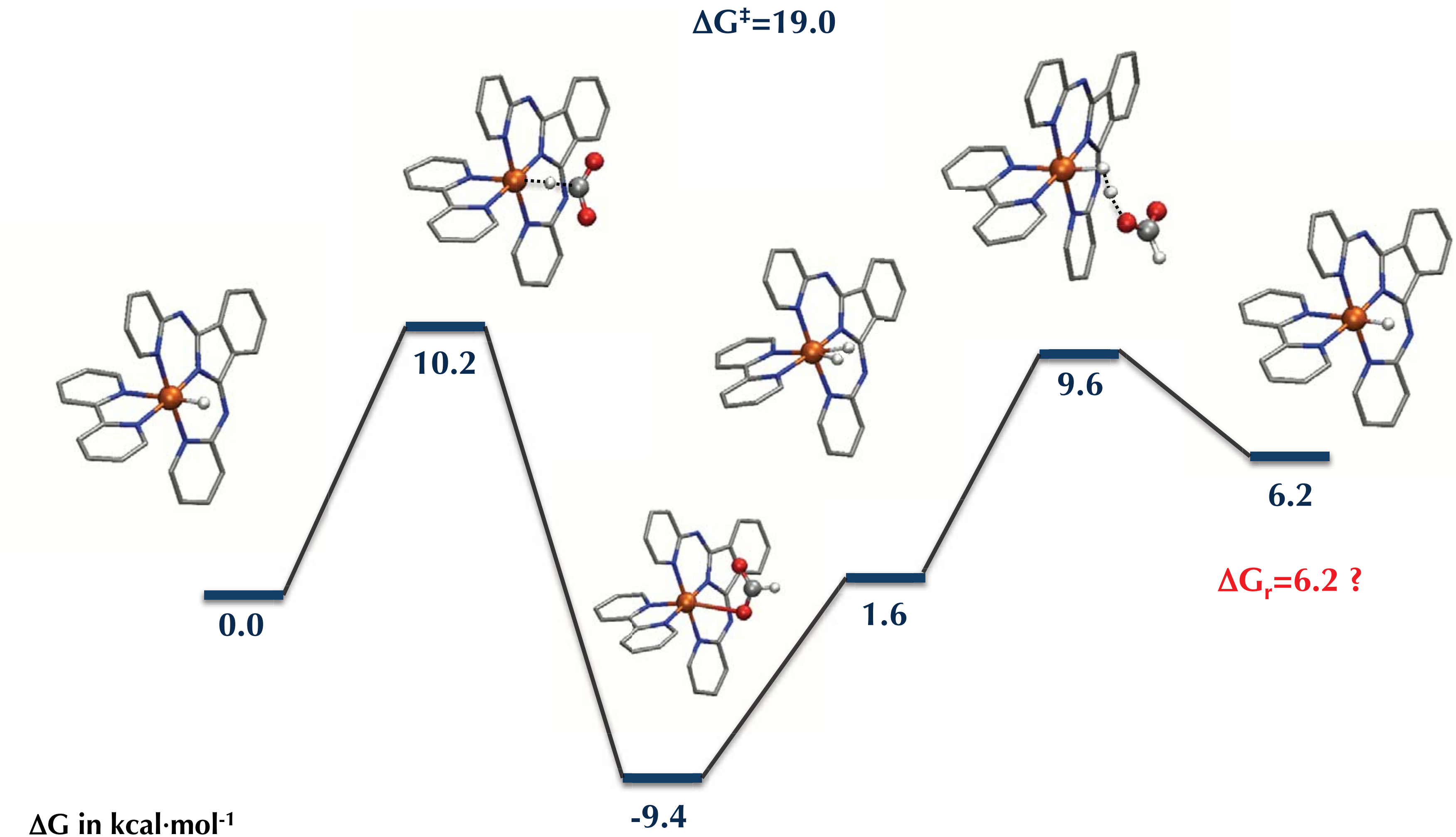
	Opt.	Single Point
Ru	SDD (ECP28MWB)	SDD (ECP28MWB)
H, C, O	6-311G(d,p)	6-311G+(2df,p)
Polypyridyl Ligands	MIDI!	

SMD continuum solvation model
(Solvent=2,2,2-TriFluoroEthanol)

All stationary points were verified
by analytic computation of vibrational frequencies

Mononuclear CO_2 Reduction Catalysts

$[Ru^{II}(H)(bid)(bpy)]$

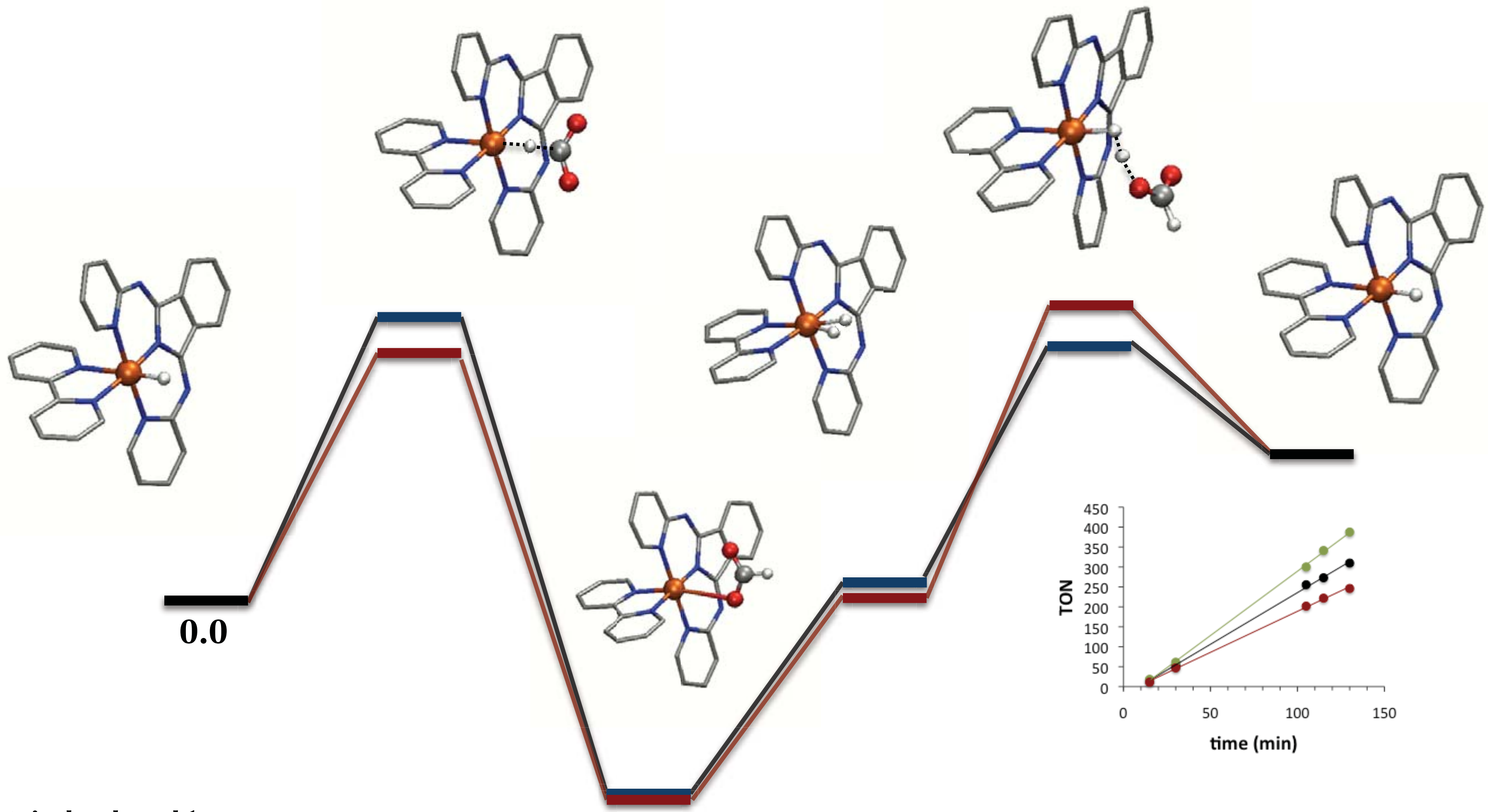


ΔG in kcal·mol^{-1}

Mononuclear CO_2 Reduction Catalysts

R = -OMe < **[Ru^{II}(H)(bid)(bpy)]**

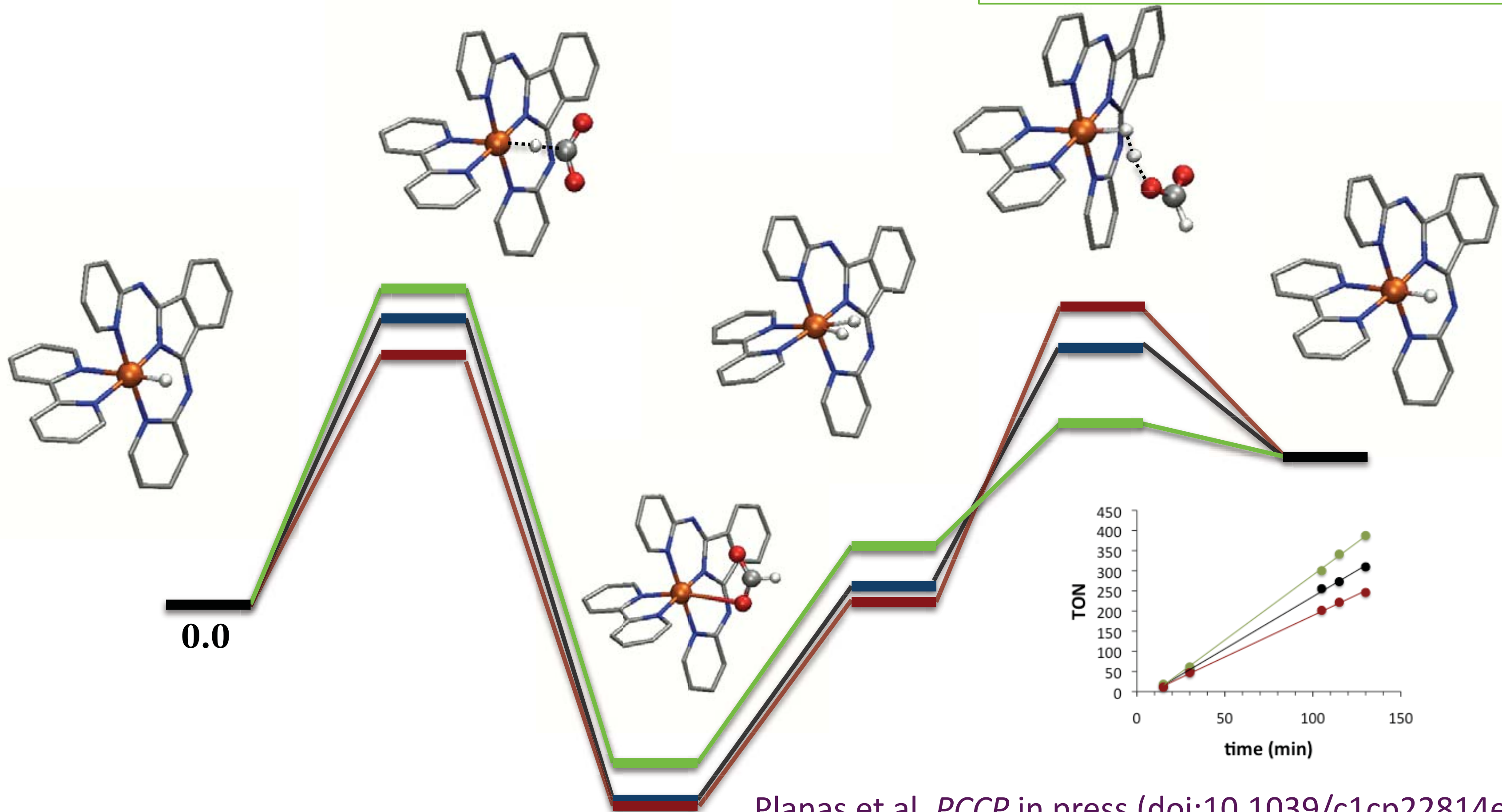
ΔG‡=20.1 **ΔG‡=19.0**



ΔG in kcal·mol^{-1}

Mononuclear CO_2 Reduction Catalysts

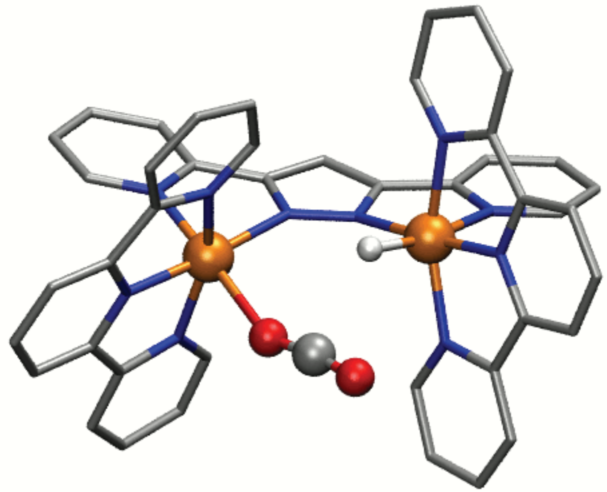
R = -OMe	<	[Ru^{II}(H)(bid)(bpy)]	<	R = -COOEt
ΔG‡=20.1		ΔG‡=19.0		ΔG‡=16.6



Planas et al. *PCCP* in press (doi:10.1039/c1cp22814e)

ΔG in kcal·mol^{-1}

Dinuclear CO_2 Reduction Catalysts



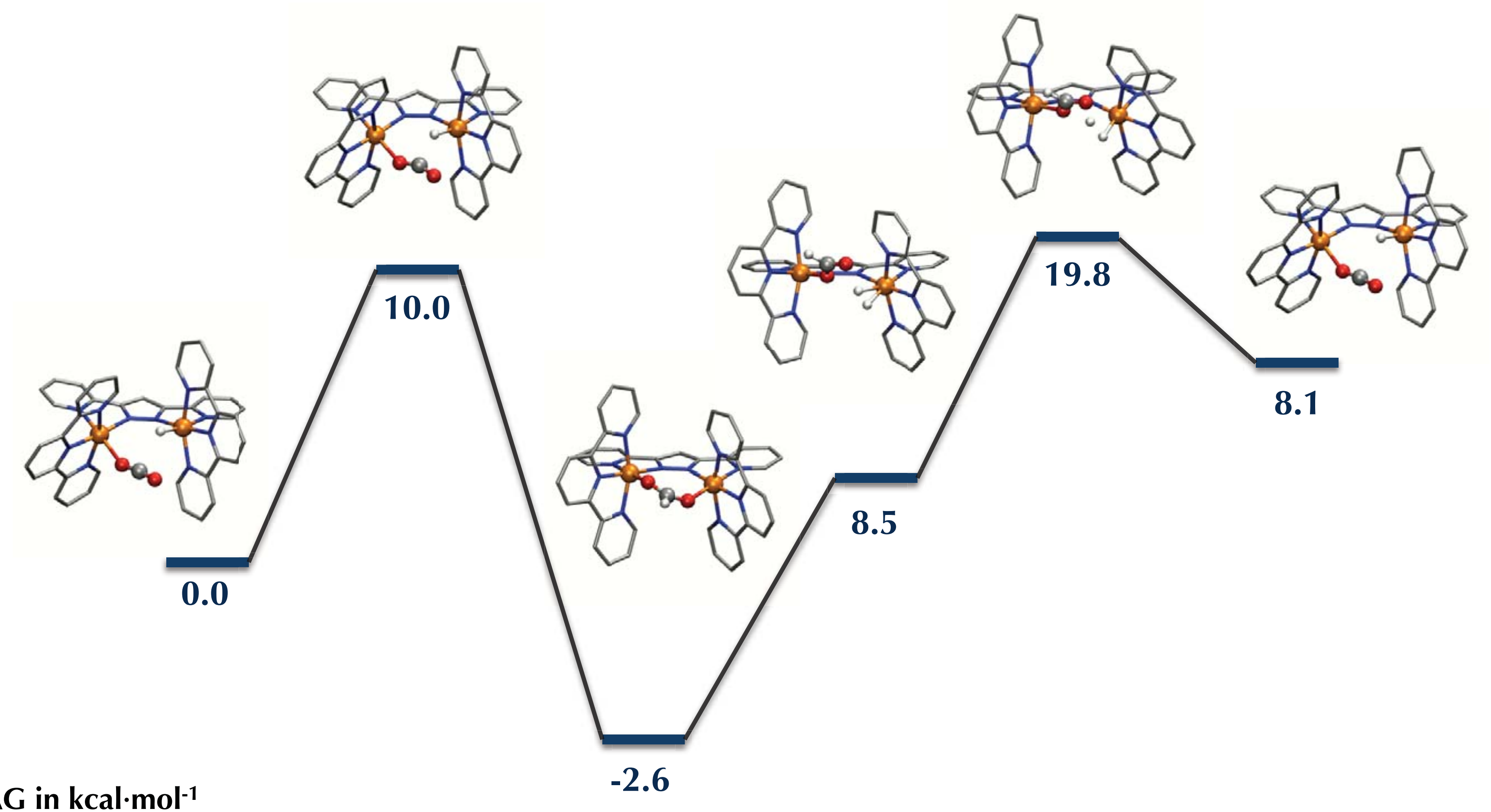
$[(Ru^{II})_2(\mu\text{-bbp})(trpy)_2(H)(CO_2)]^{2+}$

$[(Ru^{II})_2(\mu\text{-bbp})(bid)_2(H)(CO_2)]$

Dinuclear CO_2 reduction catalysts

$[(Ru^{II})_2(\mu\text{-bbp})(trpy)_2(H)(CO_2)]^{2+}$ < $[(Ru^{II})_2(\mu\text{-bbp})(bid)_2(H)(CO_2)]$

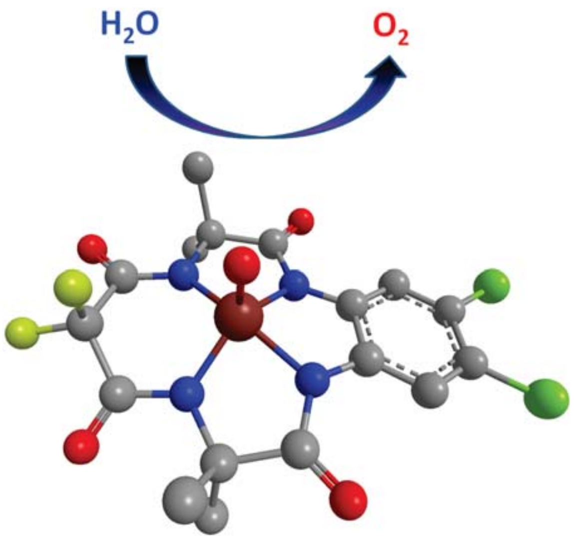
$\Delta G^{\ddagger}=22.4$ $\Delta G^{\ddagger}=20.4$

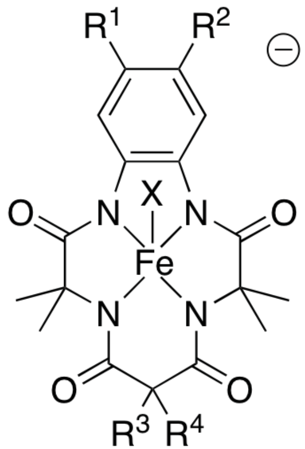


ΔG in kcal·mol^{-1}

OK, Back to Water Splitting…

A Catalyst With a Supported Earth-abundant Metal





rate-determining step ~20 kcal/mol

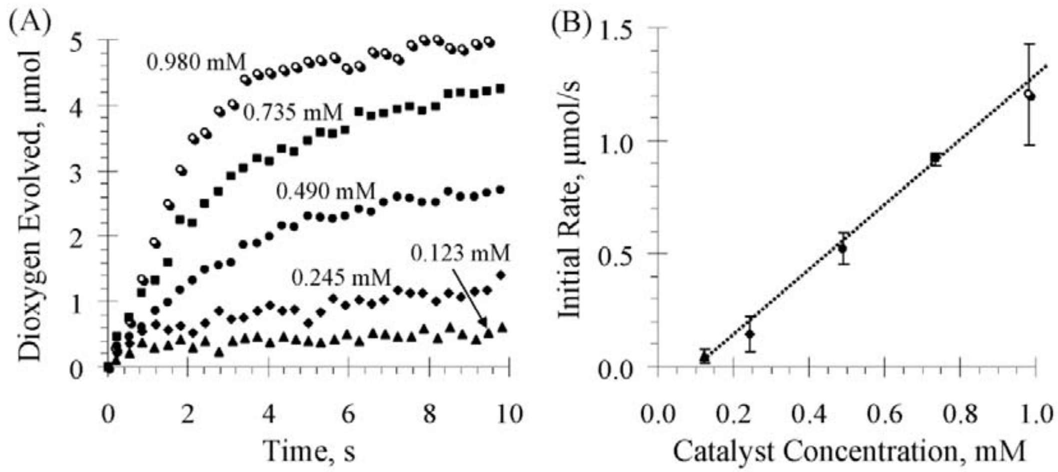
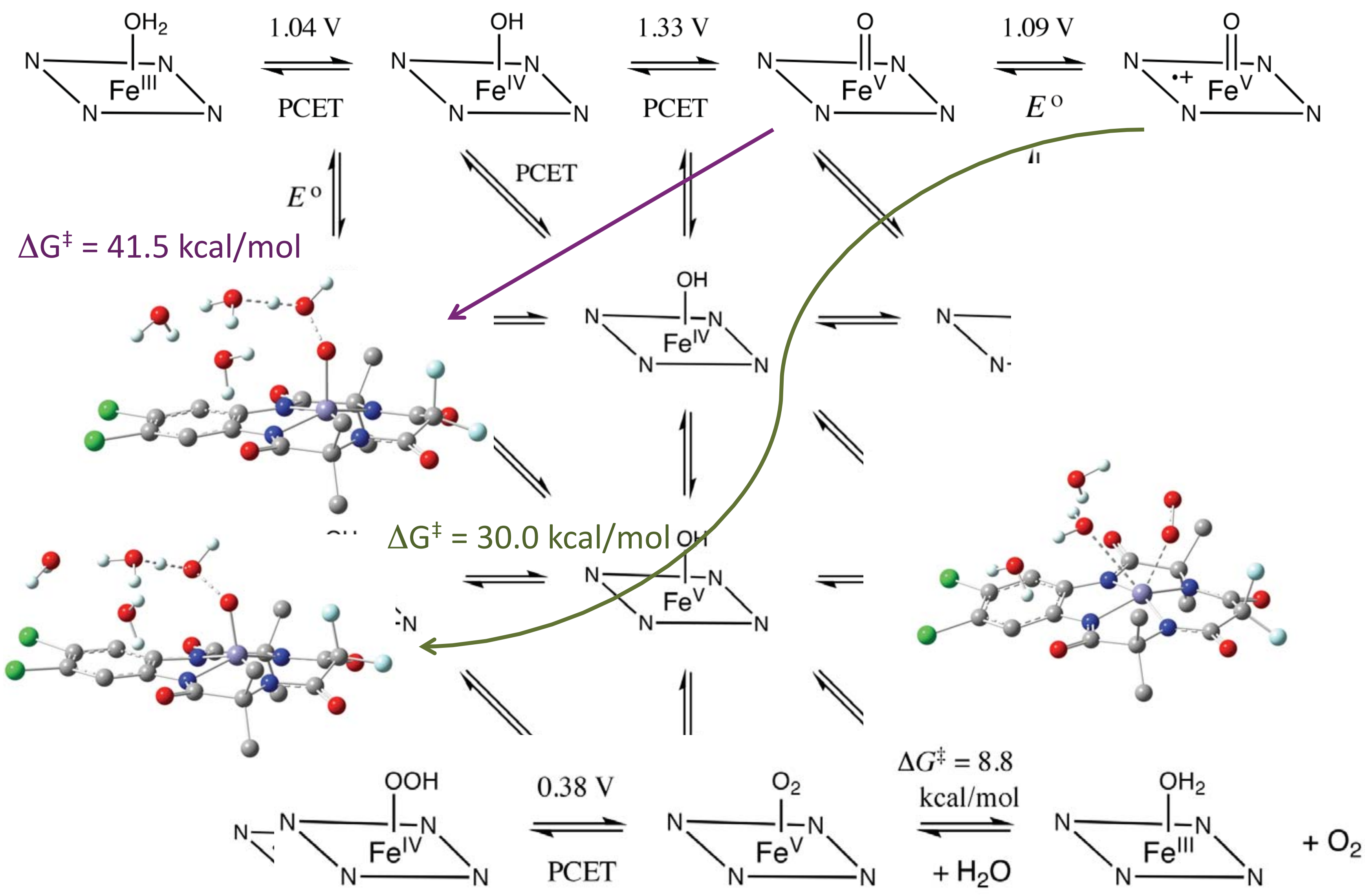


Figure 2. (A) Plots of O_2 evolution with time for different [**5**] upon addition of $(NH_4)_2Ce(NO_3)_6$ (145.7 μmol) in water (0.8 mL); the theoretical O_2 yield was 36.4 μmol. (B) Initial rates of WO plotted against [**5**].

Ellis, McDaniel, Bernhard, and Collins *J. Am. Chem. Soc.* **2010**, *132*, 10990

A Catalyst With a Supported Earth-abundant Metal



Acknowledgments

Oxygen Activation

Dr. Ben Gherman
Dr. Abdul R. Moughal Shahi
Dr. Stefan Huber
Dr. Patrick Donoghue
Dr. Joe Scanlon
David Heppner

Water Splitting/CO_2 Activ.

Dr. Pere Miró
Dr. Tanya Todorova
Zahid Ertem
Nora Planas
Stuart Kohl

Senior Collaborators

Prof. Laura Gagliardi (Geneva/Minnesota)
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Prof. Piotr Piecuch (MSU)
Prof. Bill Tolman (Minnesota)