The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

2269-17

Workshop on New Materials for Renewable Energy

17 - 21 October 2011

Ru-based water oxidation catalysts

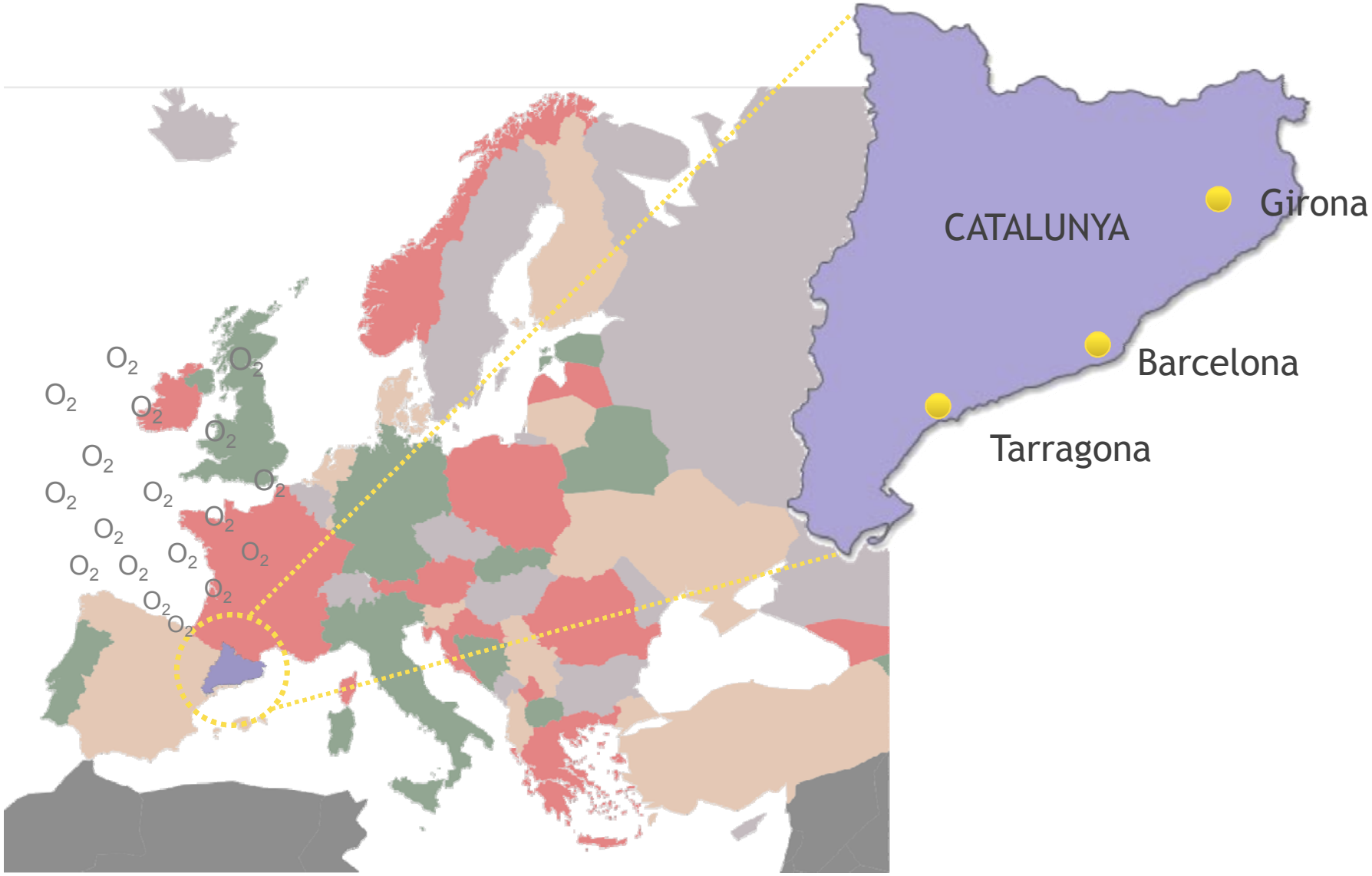
Xavier SALA
UAB
Barcelona
Spain

Ru-Based Water Oxidation Catalysts

ICTP, Miramare, Trieste, October 19th 2011

Xavier Sala, UAB, Barcelona, Spain

Where we are?



University of Girona

Dr. M. Rodríguez and Dr. I. Romero

Autonomous University of Barcelona

Dr. Xavier Sala
Dr. Lluís Escriche
Dr. Jordi García-Antón

Catalan Institute of Chemical Research

Prof. Antoni Llobet

OUTLINE

Universitat Autònoma de Barcelona

1. INTRODUCTION
2. DINUCLEAR HOMOGENEOUS WOCs
3. DINUCLEAR HETEROGENEOUS WOCs
4. TETRANUCLEAR HOMOGENEOUS WOCs
5. MONONUCLEAR WOCs: the $[Ru(bpy)_2(H_2O)_2]$ case
6. CONCLUSIONS

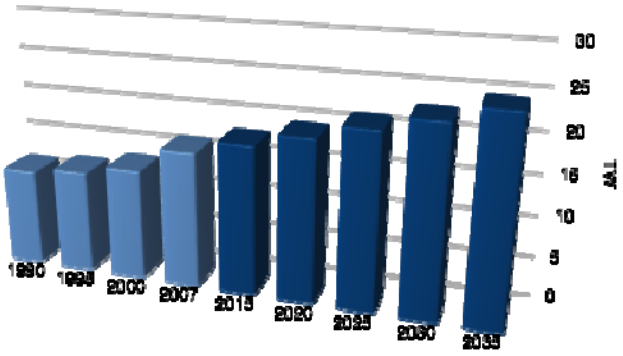
INTRODUCTION - Today's Energy Situation

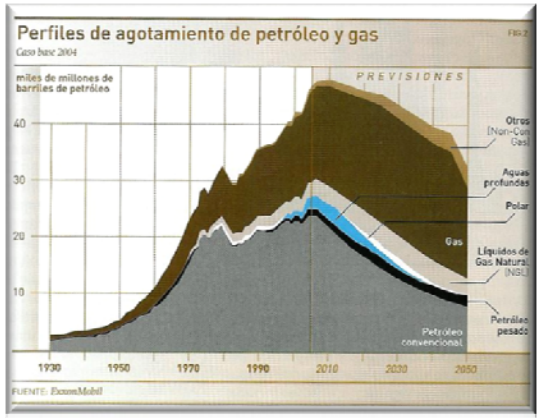
Universitat Autònoma de Barcelona

Predicted Increase of the World's Energy Demand

Exhaustion of Fossil Fuels as a Low Cost Energy Source

Impact of Anthropogenic CO_2 on the Planet





URGENT NEED OF SUSTAINABLE ENERGY SOURCES

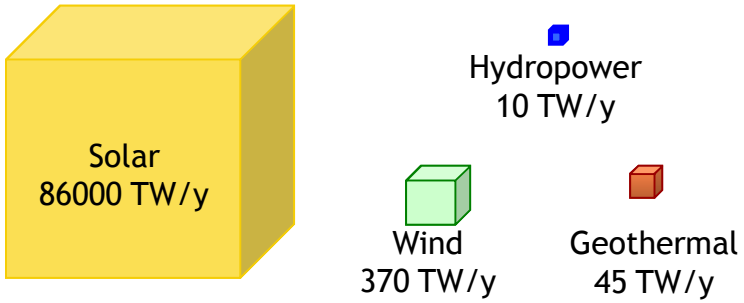
Exhausting profiles of oil products, **2004**, Exxon-Mobile.

Solar Energy Utilization Workshop, **2005**, US-DOE, Washington DC.

A. Menzel et al. *Global Change Biology*, **2006**, *12*, 1-8.

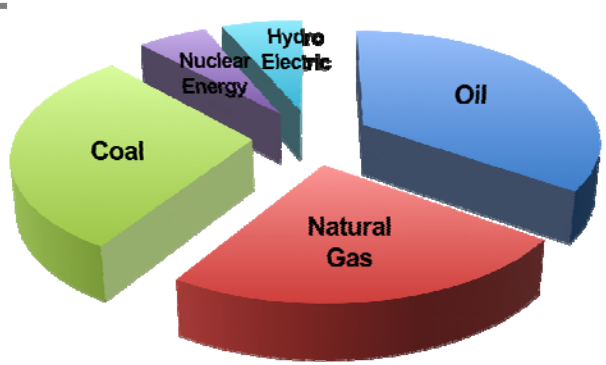
INTRODUCTION - Today's Energy Situation

Available Renewable Energy



Global Energy Consumption 2008

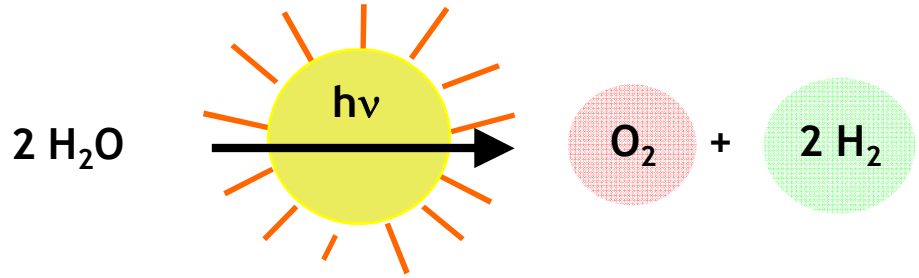
Global Energy Consumption
15 TW/y

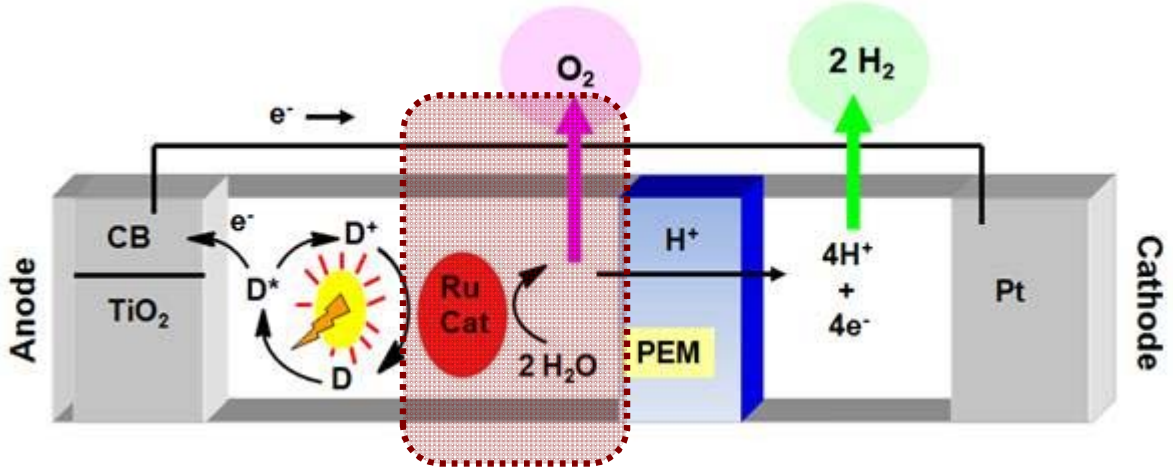


Solar Energy < 1 % (< 0.15 TW/y)

O. Morton et al. *Nature,* **2008,** *454,* 816.

BP Statistical Review of World Energy, **2009.**

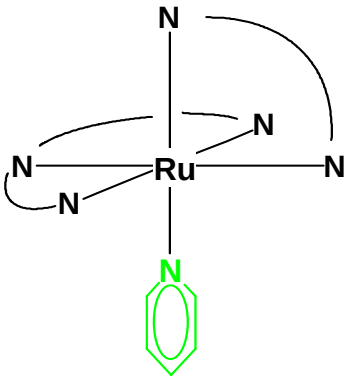




Water Oxidation

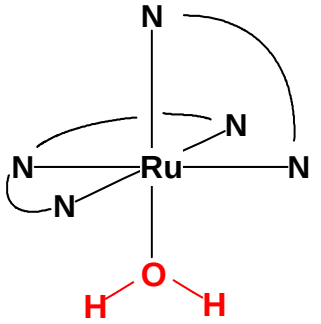
Sala, X.; Escriche, Ll.; Llobet, A. *Angew. Chem. Int. Ed.*, **2009,** 48, 2-13

INTRODUCTION –The Ru=O Group



[(trpy)(bpy)Ru-py]$^{2+}$

$E_{1/2}$ (III/II) = 1.20 V vs SSCE
$E_{1/2}$ (IV/III) = out of CV solvent range

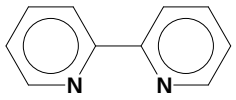


[(trpy)(bpy)Ru-H_2O]$^{2+}$

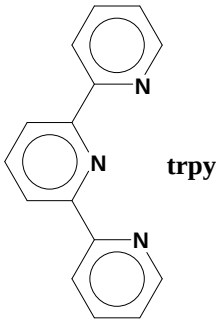
$E_{1/2}$ (III/II) = 0.49 V
$E_{1/2}$ (IV/III) = 0.62 V

Meyer,T.J. et al. *Inorg. Chem.* **1984**, 23, 1845

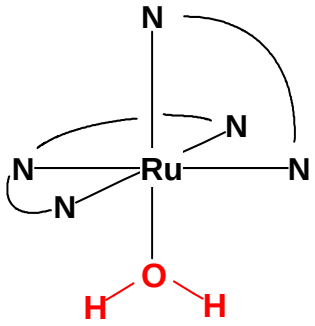
INTRODUCTION –The Ru=O Group



bpy



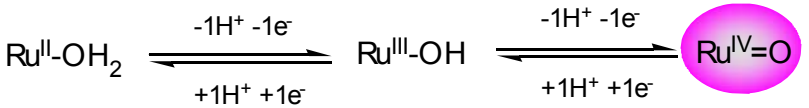
trpy



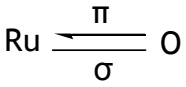
$[(trpy)(bpy)Ru\text{-}H_2O]^{2+}$

$E_{1/2}$ (III/II) = 0.49 V
$E_{1/2}$ (IV/III) = 0.62 V

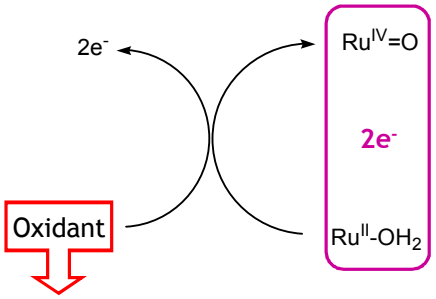
❶ Ru^{IV} stabilization



pπ (O) dπ (Ru) interaction

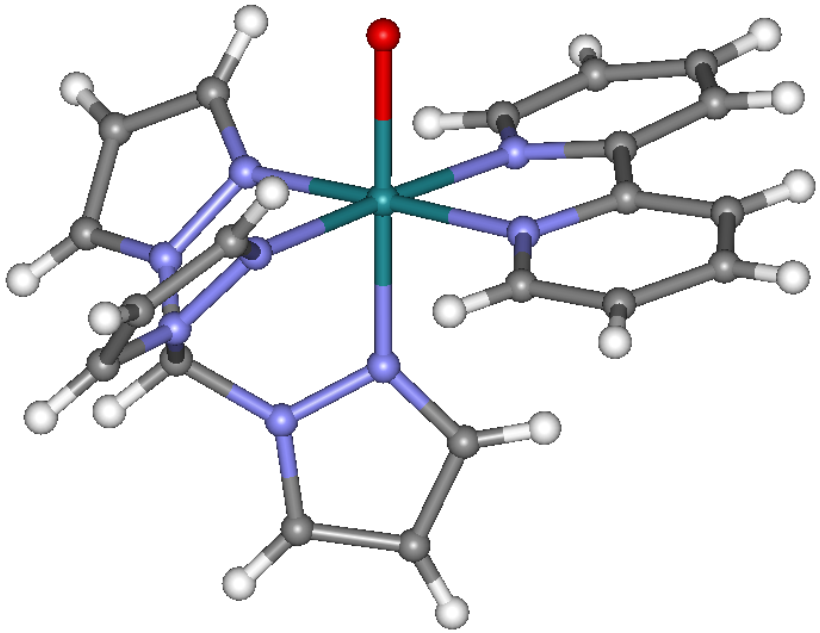


❷ Catalytic activity

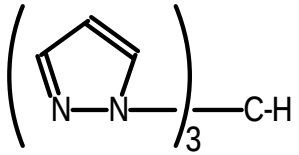


Chemical
Electrochemical
Photochemical

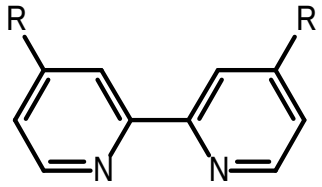
Meyer,T.J. et al. *Inorg. Chem.* 1984, 23, 1845



[(tpm)(bpy)Ru-OH_2]$^{2+}$



tpm



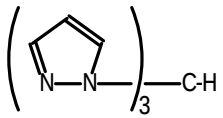
4,4'-R_2-bpy

R=H,bpy
R=NH_2,b-NH_2
R=NO_2,b-NO_2

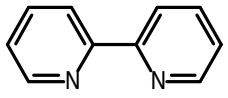
Llobet, A. *Inorg. Chim. Acta* **1994** 221, 125-131.
Sala, X.; Rodríguez, M.; Romero, I.; Llobet, A. et al. *Inorg. Chem.* **2007** 110, 7751-7759.

$\Delta E = E_{1/2}(IV/III) - E_{1/2}(III/II)$ in mV

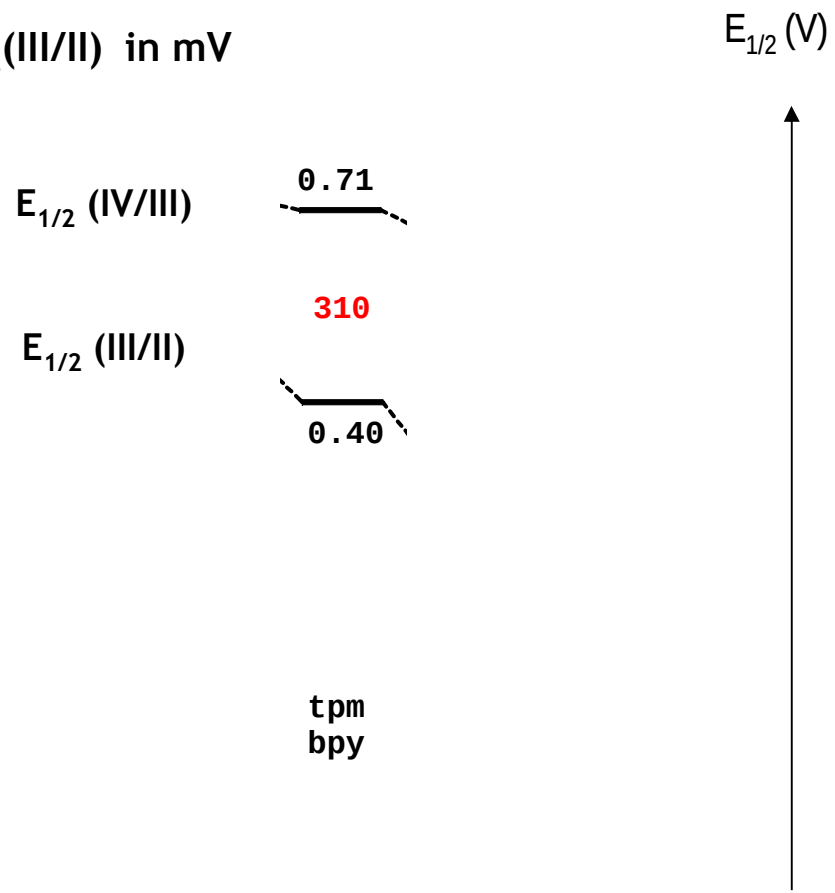
$[(tpm)(bpy)Ru\text{-}OH_2]^{2+}$



tpm



bpy



$E_{1/2}$ (V vs SSCE) at pH = 7.0

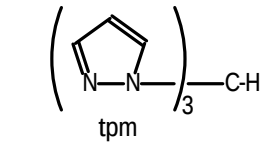
Llobet, A. *Inorg. Chim. Acta* **1994** 221, 125-131.

Sala, X.; Rodríguez, M.; Romero, I.; Llobet, A. et al. *Inorg. Chem.* **2007** 110, 7751-7759.

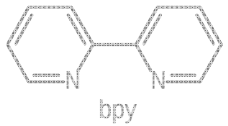
INTRODUCTION -The Ru=O Group

$\Delta E = E_{1/2}(IV/III) - E_{1/2}(III/II)$ in mV

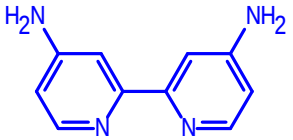
$[(tpm)(b\text{-}NH_2)Ru\text{-}OH_2]^{2+}$



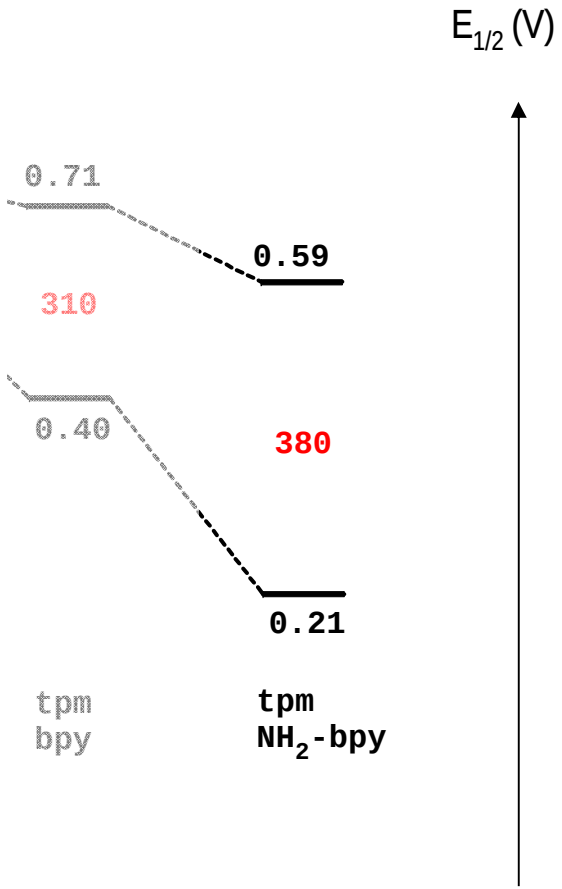
tpm



bpy



b-NH2



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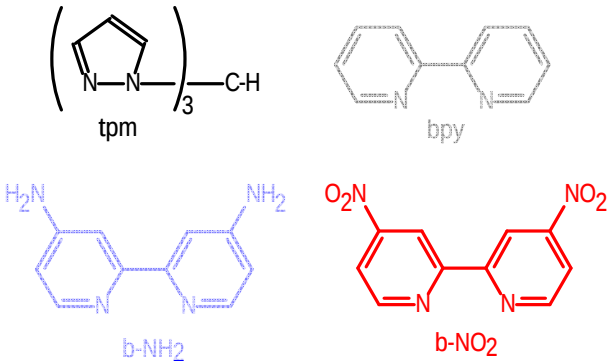
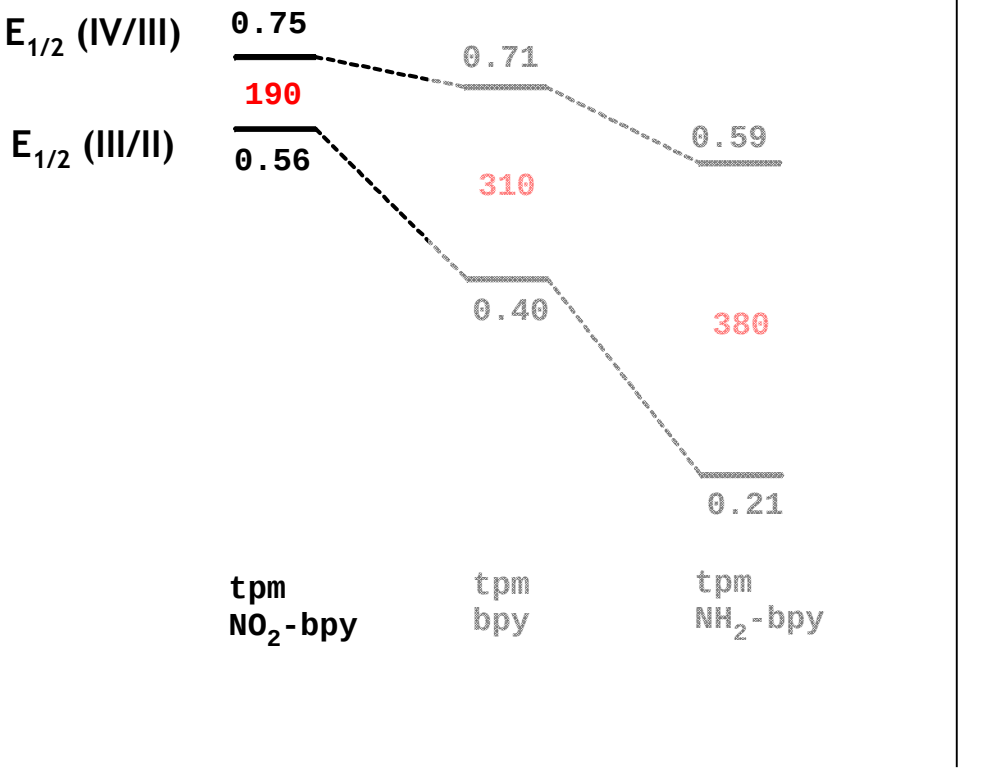
Sala, X.; Rodríguez, M.; Romero, I.; Llobet, A. et al. *Inorg. Chem.* **2007** 110, 7751-7759.

$\Delta E = E_{1/2}(IV/III) - E_{1/2}(III/II)$ in mV

$[(tpm)(b\text{-}NO_2)Ru\text{-}OH_2]^{2+}$



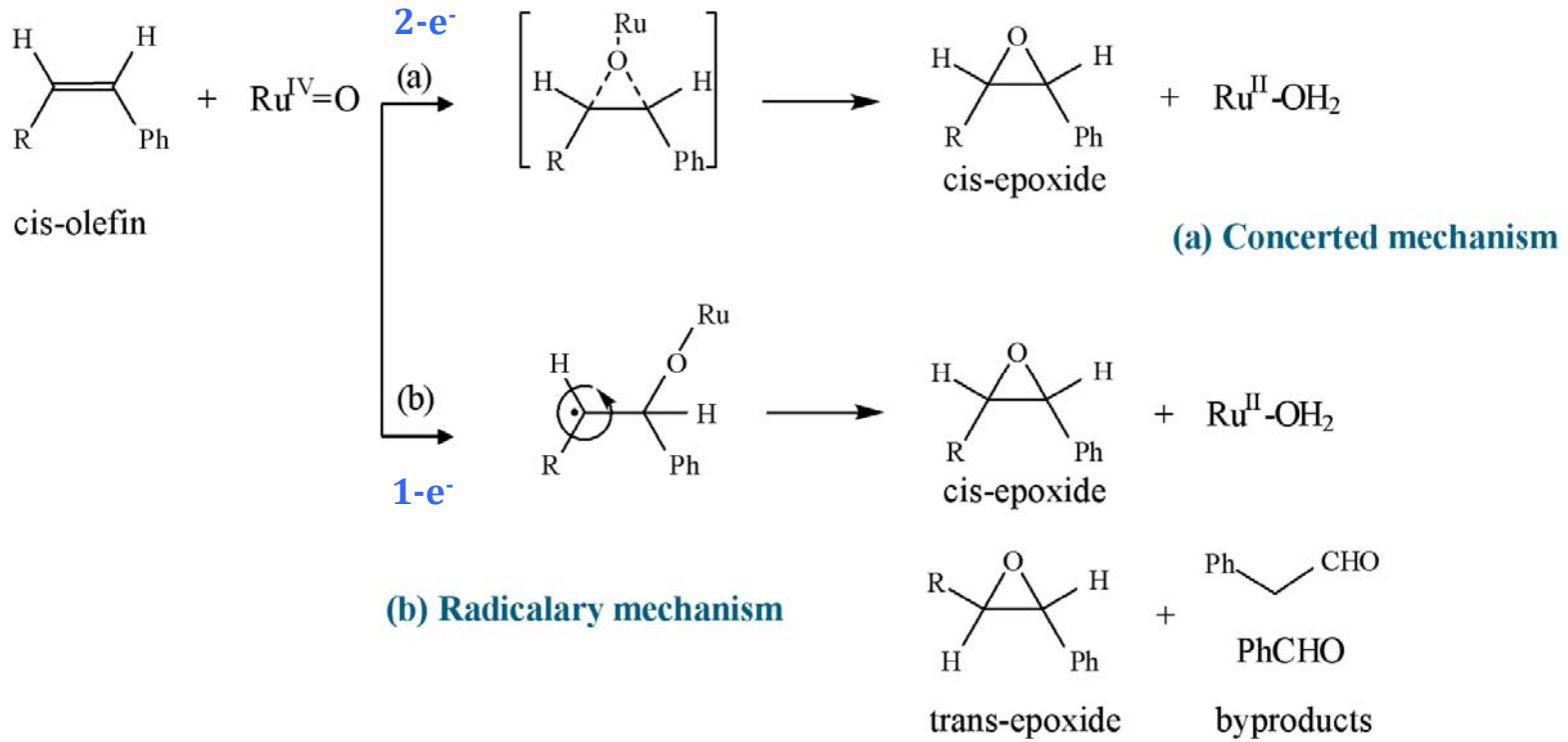


$E_{1/2}$ (V vs SSCE) at pH = 7.0

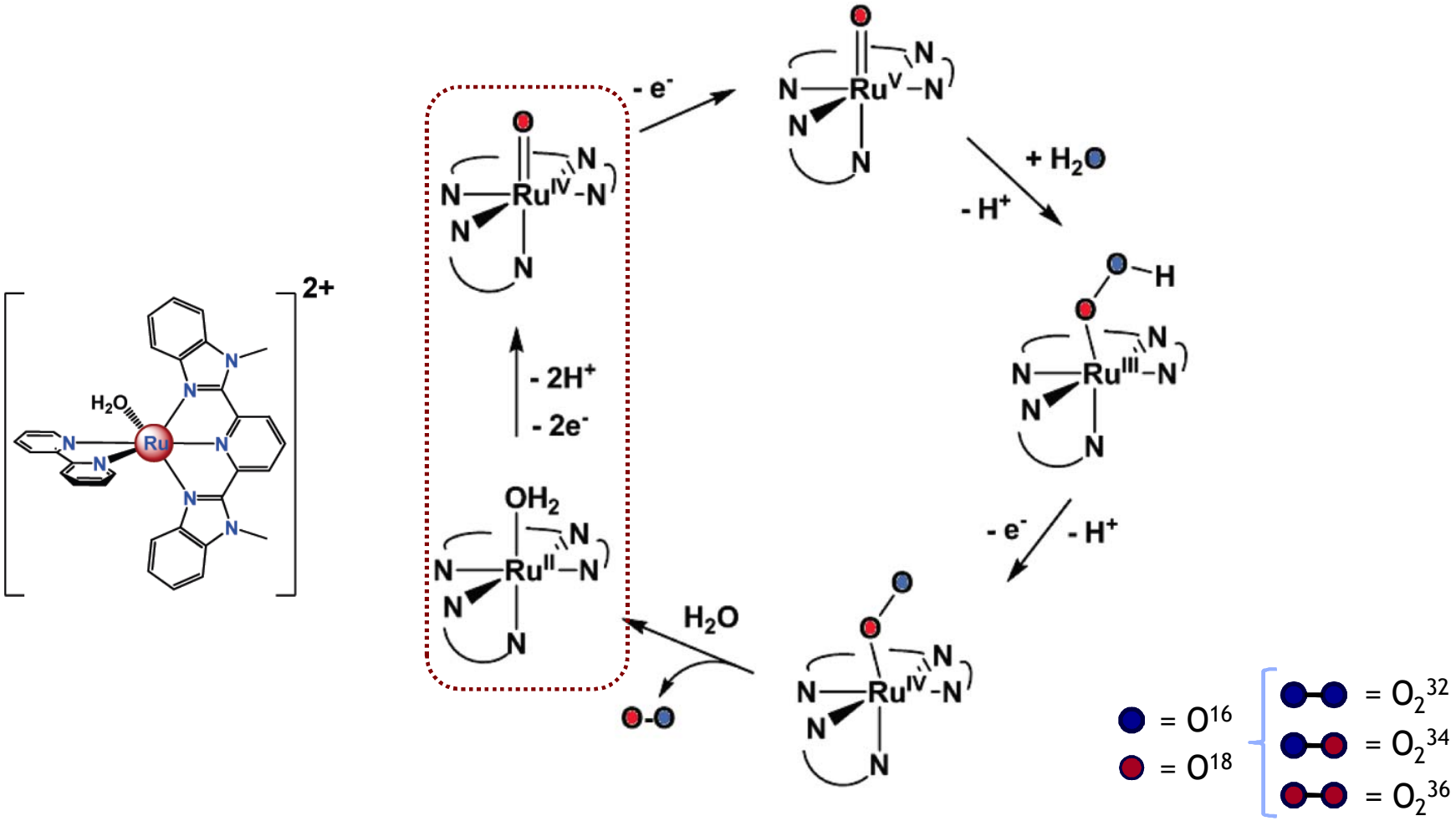
Llobet, A. *Inorg. Chim. Acta* **1994** 221, 125-131.

Sala, X.; Rodríguez, M.; Romero, I.; Llobet, A. et al. *Inorg. Chem.* **2007** 110, 7751-7759.

- 2-electron *vs.* 1-electron oxidation ⟹ SELECTIVITY

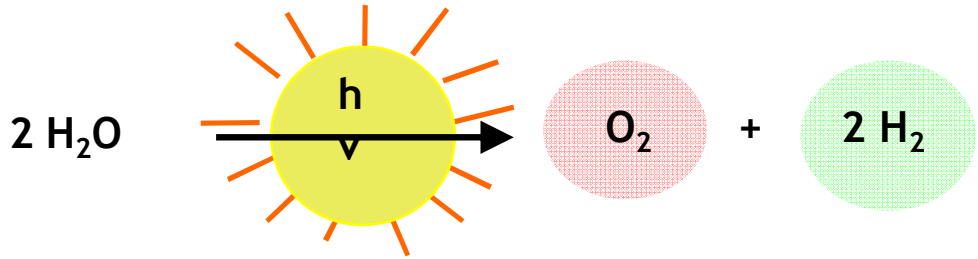


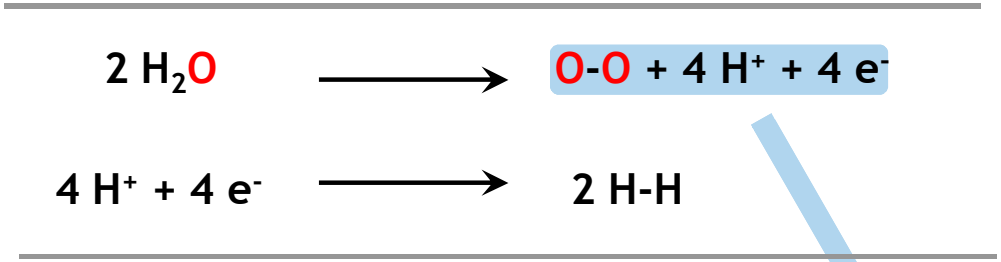
Masllorens, E.; Llobet, A. et al. *J. Am. Chem. Soc.* **2006,** 128, 5306.
Che, C.-M. et al. *J. Org. Chem.* **1998**, 63, 7715

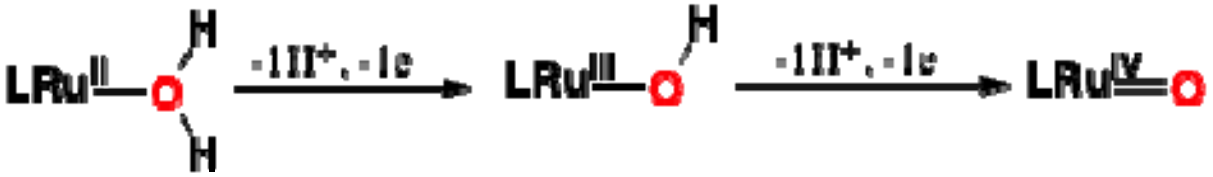


Concepcion, J. J.; Meyer, T. J. et al. J. Am. Chem. Soc. **2008**, 130, 16462
Concepcion, J. J.; Meyer, T. J. et al. J. Am. Chem. Soc. **2010**, 132, 1545

INTRODUCTION -The Ru=O Group and WO







Meyer, T. J. et al. *Inorg. Chem.* **1984**, 23, 1845

$$H_2O\text{-}^{II}Ru\text{—}BL\text{—}Ru^{II}\text{-}OH_2$$

BL: Bridging Ligand

Electronic Coupling between Ru

Interactions Through Space

OUTLINE

Universitat Autònoma de Barcelona

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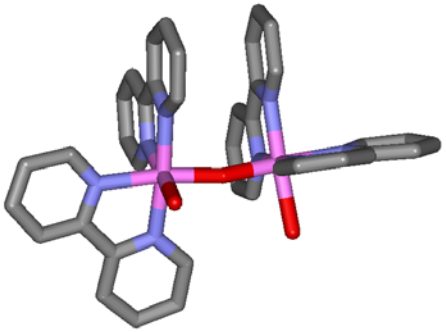
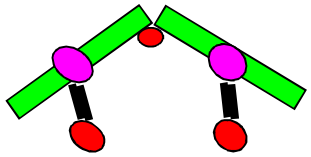
5. MONONUCLEAR WOCs: the $[Ru(bpy)_2(H_2O)_2]$ case
6. CONCLUSIONS

HOMOGENEOUS WOCs: Ru-Hbpp complexes

2 X

$[(bpy)_2Ru^{V}\text{-}O\text{-}Ru^{V}(bpy)_2]^{4+}$

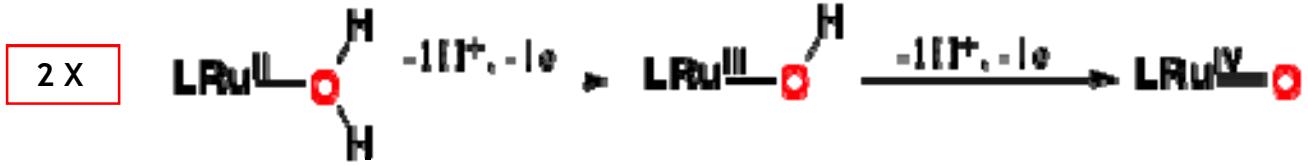




Gestern, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.*, **1982,** *104*, 4029

Gilbert, J. A.; Eggleston, D. S.; Meyer, T. J. et al. *J. Am. Chem. Soc.*, **1985,** *107*, 3855

HOMOGENEOUS WOCs: Ru-Hbpp complexes

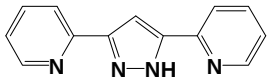


$[(trpy)Ru^{II}\text{-}(bpp)\text{-}Ru^{II}(trpy)]^{3+}$

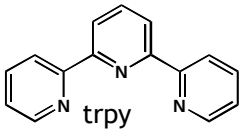
H_2O OH_2

$[(bpy)_2Ru^{V}\text{-}O\text{-}Ru^{V}(bpy)_2]^{4+}$

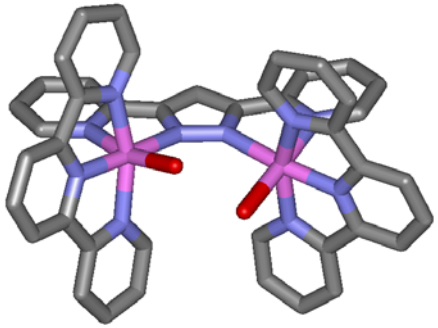
O O

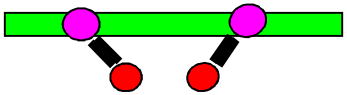


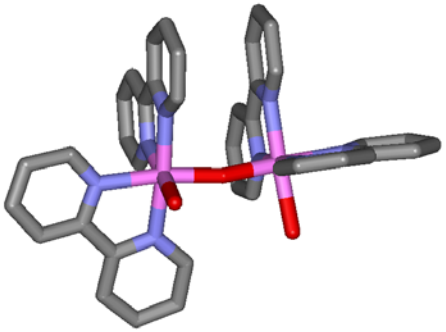
Hbpp

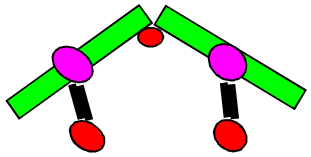


trpy





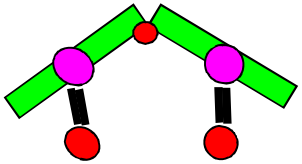


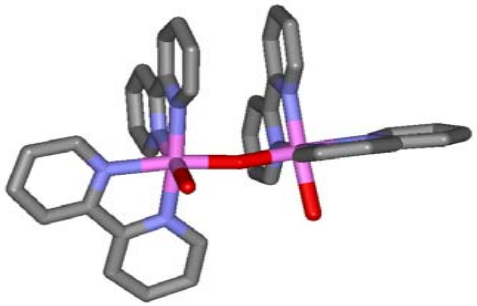


Sens, C., Llobet, A., *J. Am. Chem. Soc.*, **2004**, 126, 7798

HOMOGENEOUS WOCs: Ru-Hbpp complexes

1 mM Cat/100 mM Ce(IV)/0.1 M triflic acid/RT





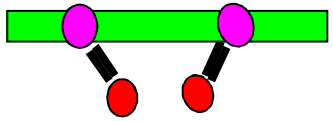
$[(bpy)_2Ru^{III}\text{-}O\text{-}Ru^{III}(bpy)_2]^{4+}$

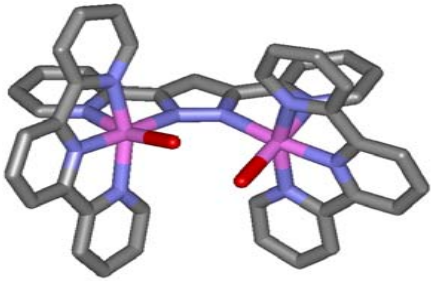
H_2O OH_2

	k_{O2} (s^{-1})	TON	Eff (%)
Blue dimer	$4.2x10^{-3}$	4-5 (25)	16-20
Hbpp	$1.4x10^{-2}$	18.5 (25)	74

Ce(IV)

WOC : Ce(IV) 1:100





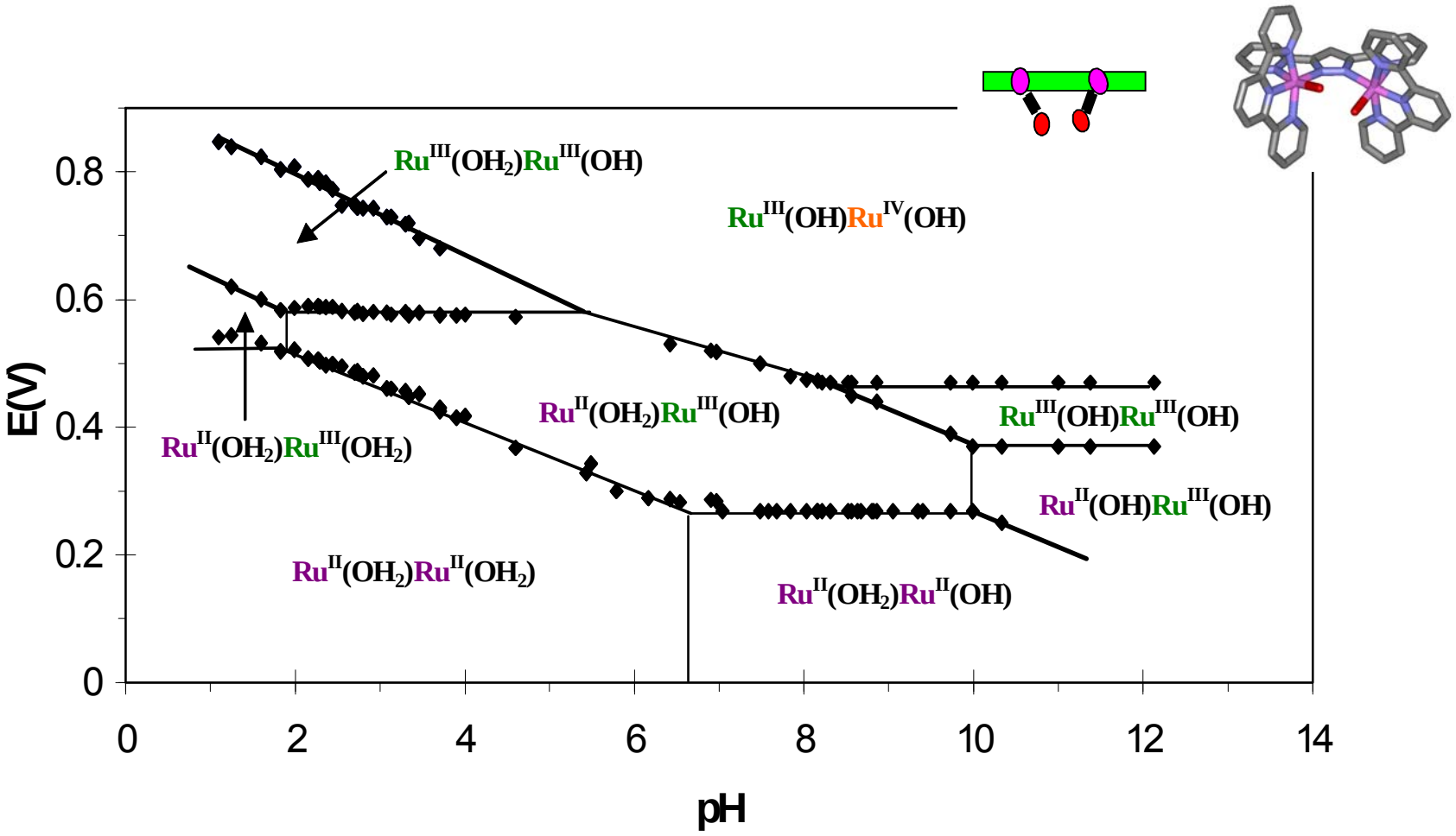
$[(trpy)Ru^{II}\text{-}(bpp)\text{-}Ru^{II}(trpy)]^{3+}$

H_2O OH_2

Gilbert, J. A.; Eggleston, D. S.; Meyer, T. J. et al. *J. Am. Chem. Soc.*, **1985,** *107*, 3855

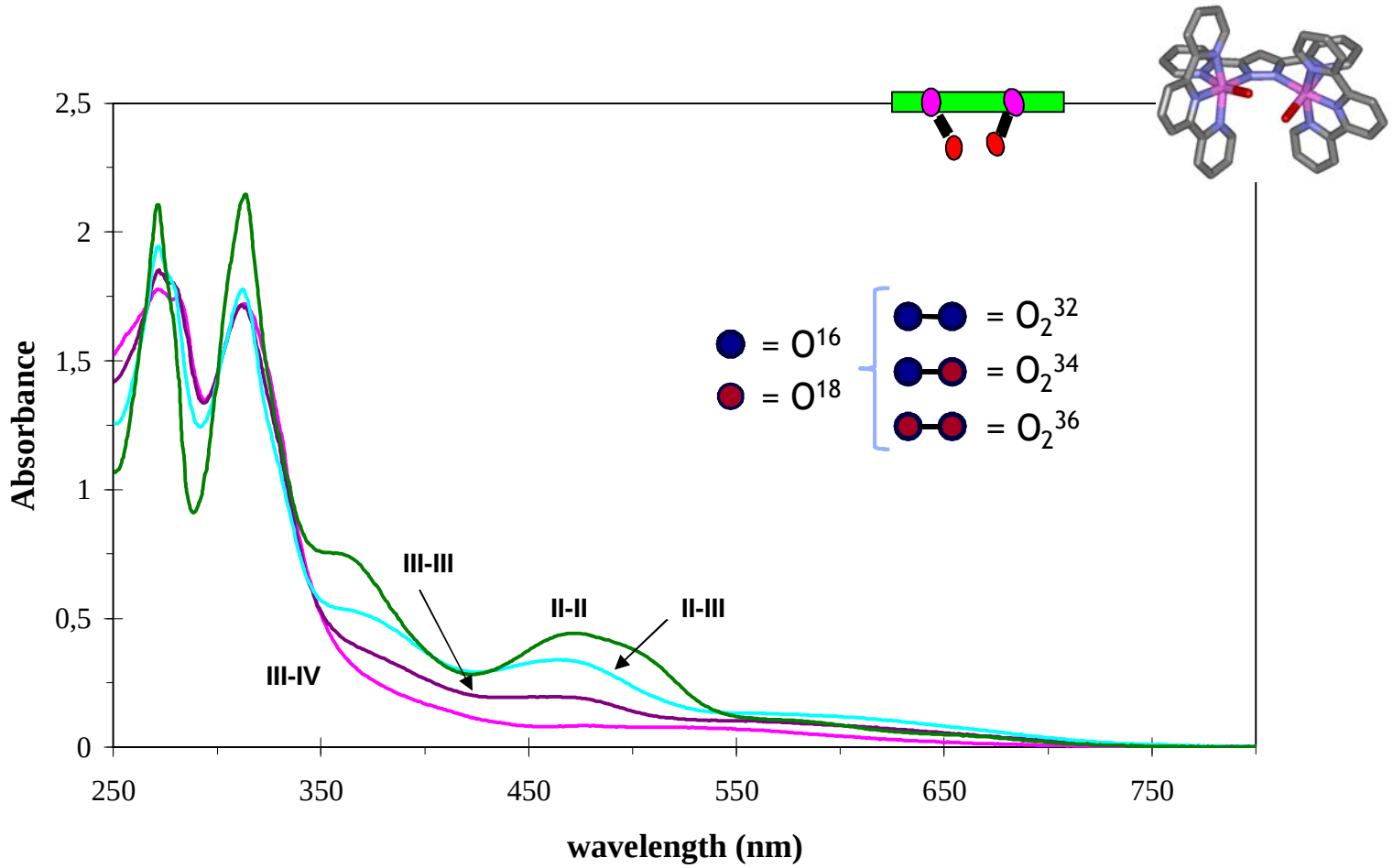
Sens, C., Llobet, A., *J. Am. Chem. Soc.*, **2004**, 126, 7798

HOMOGENEOUS WOCs: Ru-Hbpp complexes – ECHEM



Sens, C., Llobet, A., *J. Am. Chem. Soc.*, **2004**, 126, 7798

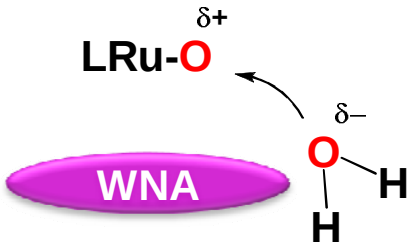
HOMOGENEOUS WOCs: Ru-Hbpp complexes – UV-vis

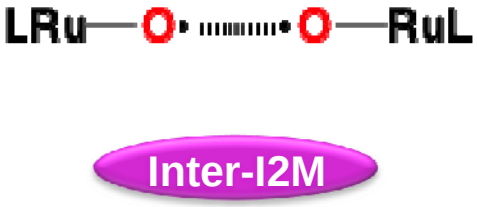


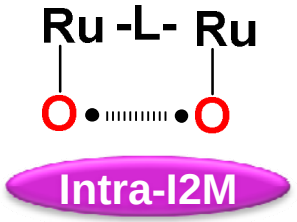
Sens, C., Llobet, A., *J. Am. Chem. Soc.*, **2004**, 126, 7798

O-O Coupling Pathways

Water Nucleophilic Attack	Intermolecular O-O Coupling	Intramolecular O-O Coupling

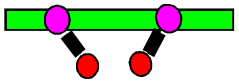




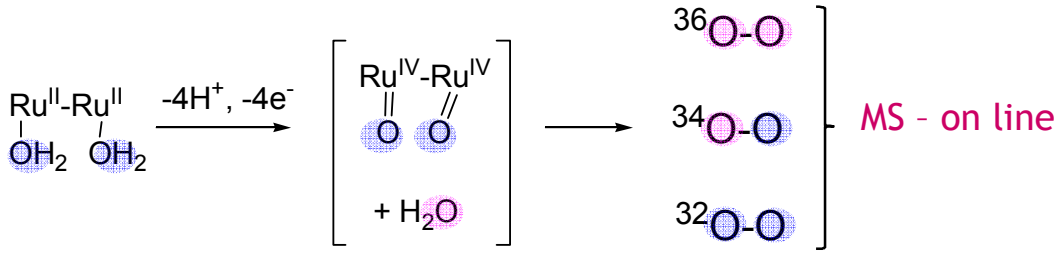


T. J. Meyer et al., *Inorg. Chem.* **2003**, *42*, 8140.

A. Llobet et al., *Acc. Chem. Res.* **2009**, *42*, 1944.

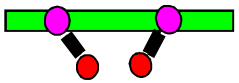


O_2-evolution: cat with no labeling, solvent with O^{18}

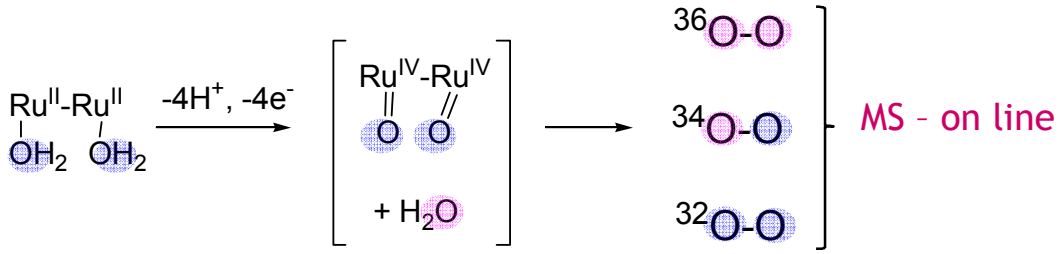


Entry	O^{18} (%)		Exchange	WNA	Intra-I2M	Exp.
1	Cat, -- Solv, 12.00	$^{32}O_2$				99,50
2		$^{34}O_2$				0,47
3		$^{36}O_2$				0,03

Romain, S.; Sala, X.; Llobet, A. et al. *J. Am. Chem. Soc.* **2009**, 131, 2768-2769



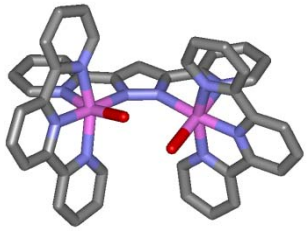
O_2-evolution: labeling the cat O^{16}/O^{18} with H_2O^{16}/H_2O^{18}

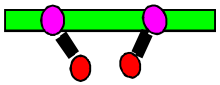


Entry	O^{18} (%)		Exchange	WNA	Intra-I2M	Exp.
4	Cat, 16.13 Solv, 11.90	$^{32}O_2$	77.60	74.60	70.34	69.97
5		$^{34}O_2$	21.00	14.50	27.05	27.48
6		$^{36}O_2$	1.40	1.90	2.61	2.55

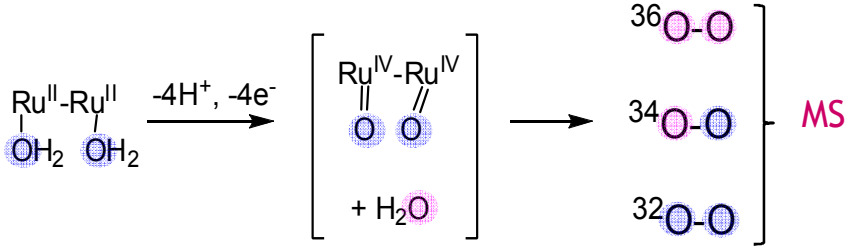
Romain, S.; Sala, X.; Llobet, A. et al. *J. Am. Chem. Soc.* **2009**, 131, 2768-2769

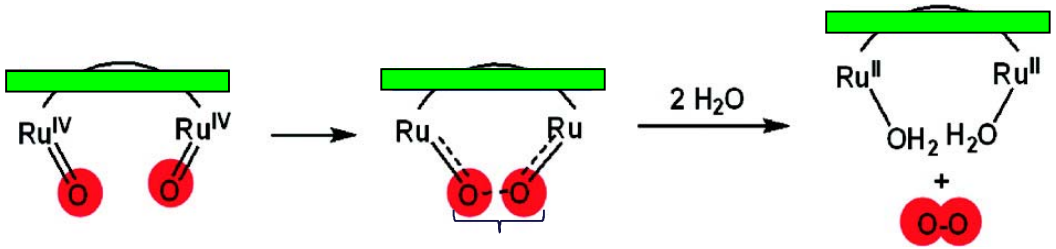
HOMOGENEOUS WOCs: Ru-Hbpp complexes: O-O bond formation





: mechanistic studies





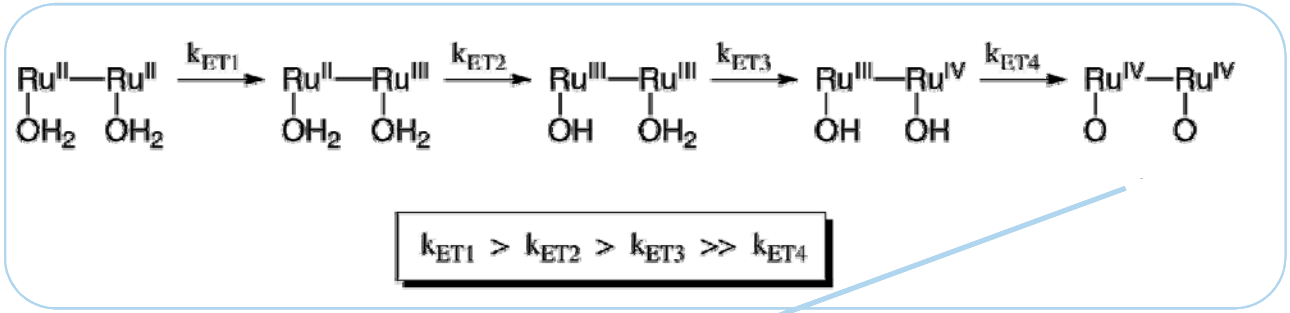
100 % INTRA-molecular

(1st direct evidence)

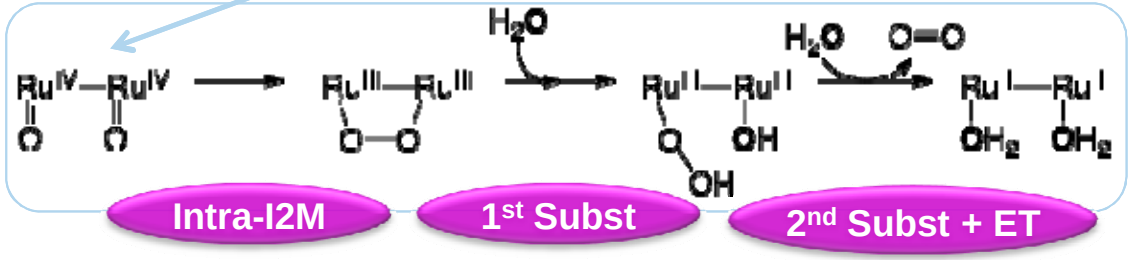
Romain, S.; Sala, X.; Llobet, A. et al. *J. Am. Chem. Soc.* **2009**, 131, 2768-2769

HOMOGENEOUS WOCs: Ru-Hbpp complexes: O-O bond formation

Electron Transfer Processes



Intramolecular O-O bond formation Mechanism



Romain, S.; Sala, X.; Llobet, A. et al. *J. Am. Chem. Soc.* **2009**, 131, 2768-2769

Bozoglian, F.; Romain, S.; Llobet, Cramer, C.; Gagliardi, L. et al. *J. Am. Chem. Soc.* **2009**, 131, 2768-2769

HOMOGENEOUS WOCs: Ru-Hbpp complexes – Dynamic Behavior

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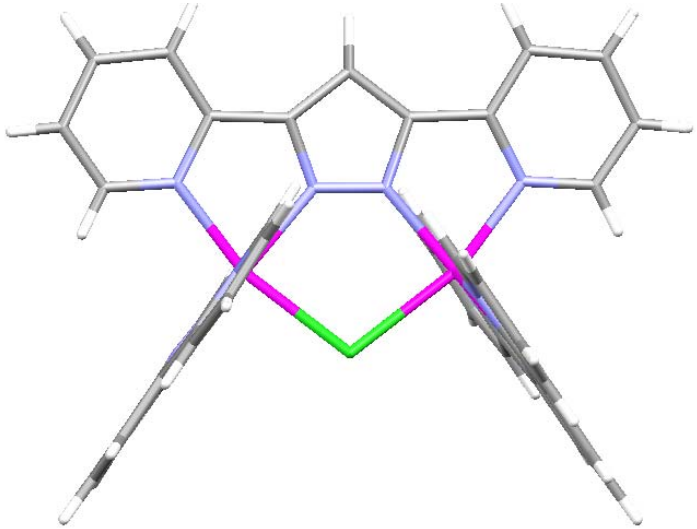
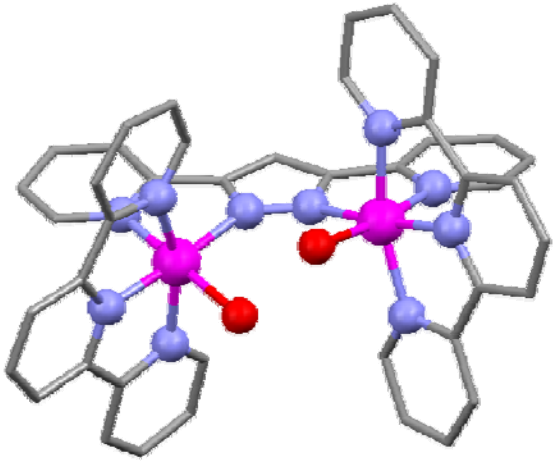
Rigid Molecule: NO dynamic behavior



C_{2v} **symmetry**

d(Ru-Ru) = 3.88 Å

Flexible Molecule: dynamic behavior

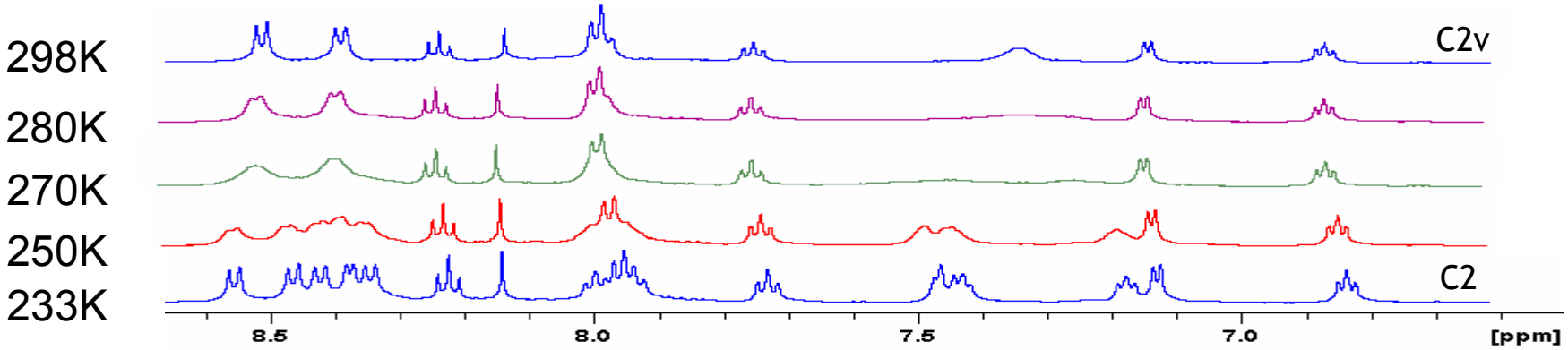


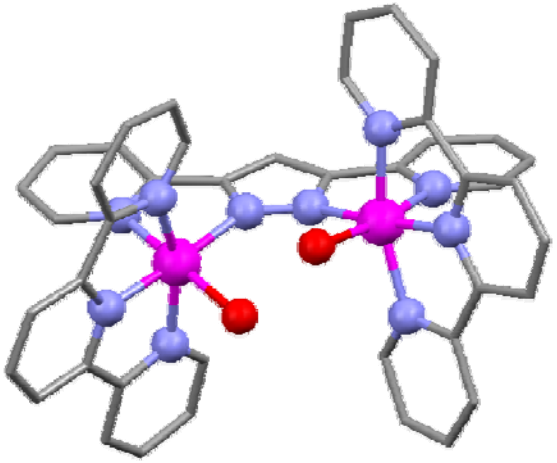
C_2 **symmetry**

d(Ru-Ru) = 4.53 Å

Planas, N.; Maseras, F.; Sala, X.; Llobet, A. et al. *Chem. Eur. J.* **2010**, *1, 284.*

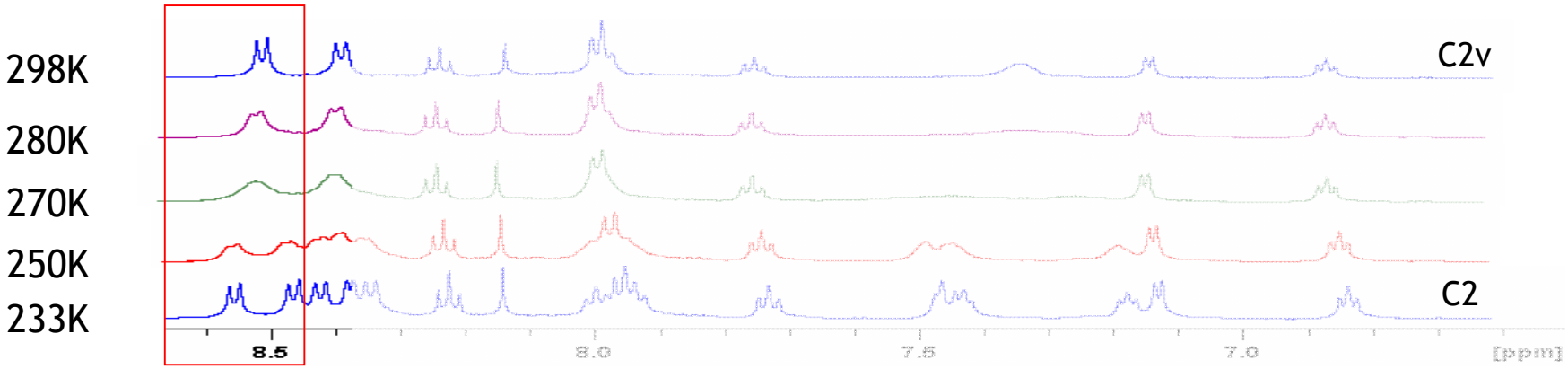
HOMOGENEOUS WOCs: Ru-Hbpp c<omplexes – Dynamic Behavior

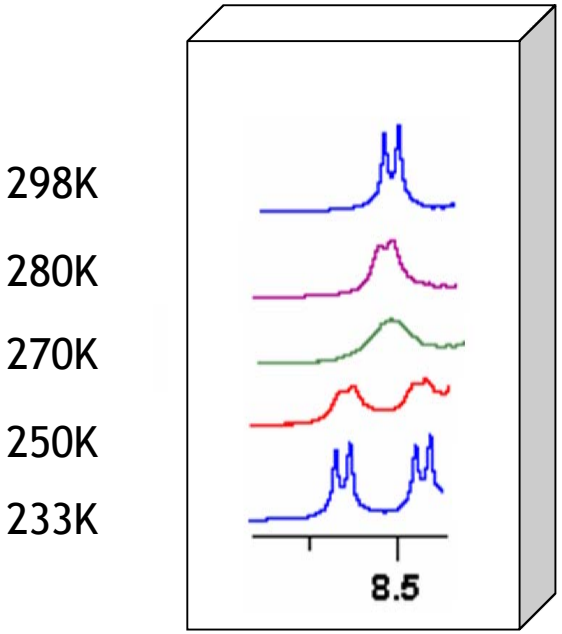


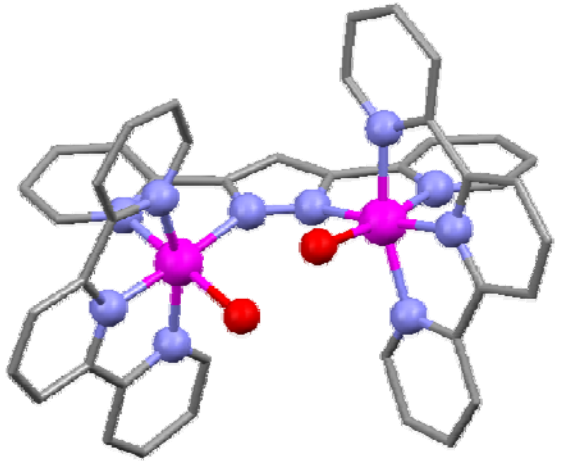


Planas, N.; Maseras, F.; Sala, X.; Llobet, A. et al. *Chem. Eur. J.* **2010**, *1(3), 284.*

HOMOGENEOUS WOCs: Ru-Hbpp complexes – Dynamic Behavior

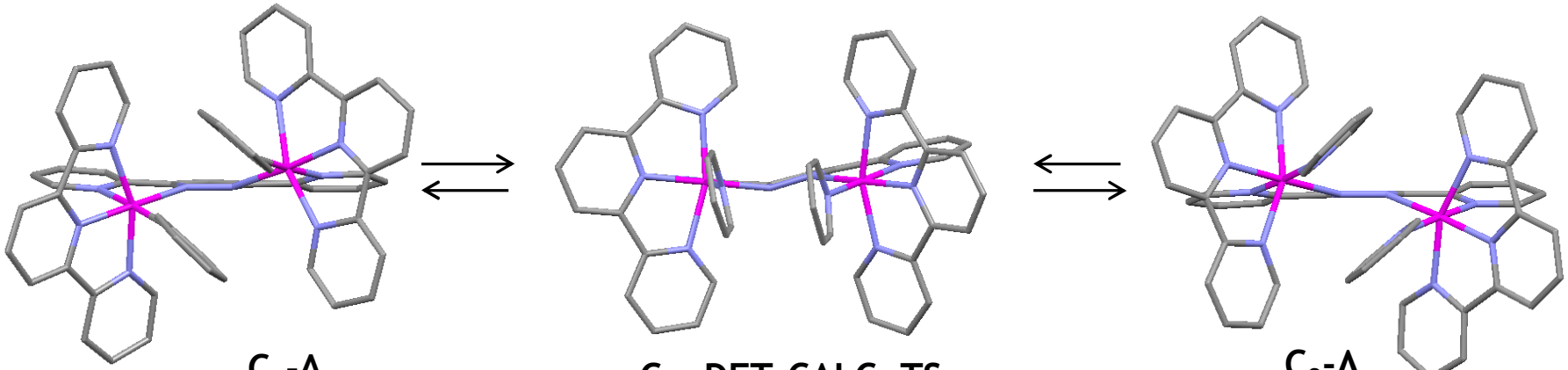




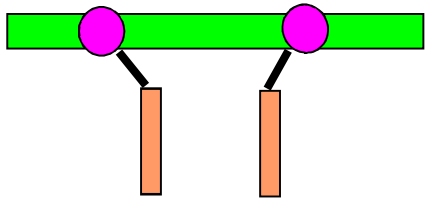


Planas, N.; Maseras, F.; Sala, X.; Llobet, A. et al. *Chem. Eur. J.* **2010**, *1(3), 284.*

HOMOGENEOUS WOC: Ru-Hbpp complexes – Dynamic Behavior

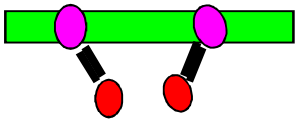


C_2-Δ C_{2v}-DFT-CALC. TS C_2-Λ

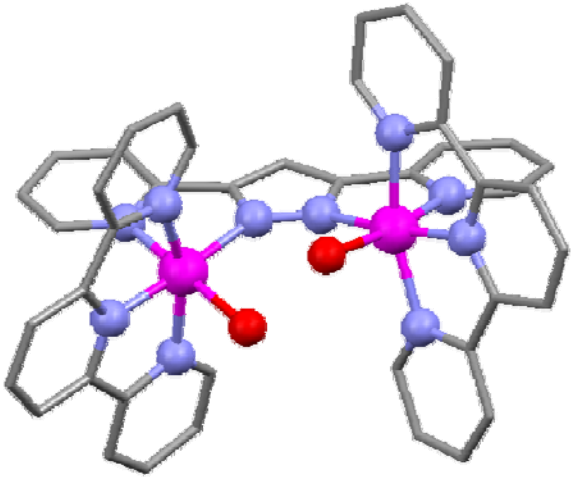


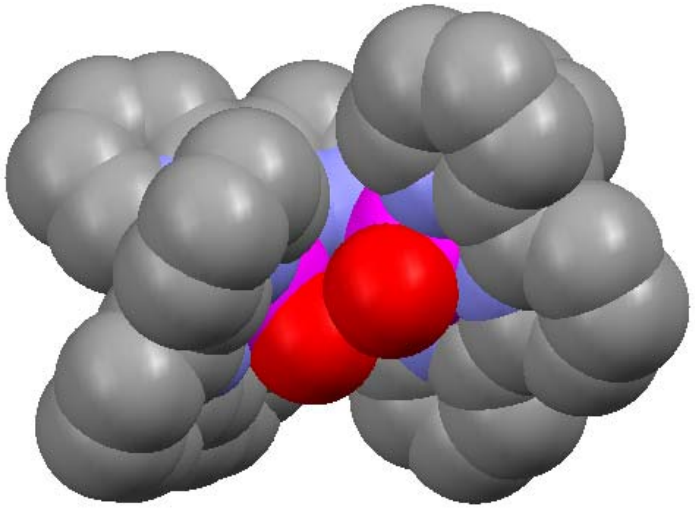
L =	ΔG*	
Py	10.0	kcal/mol
4-Me-py	10.8	
2,6-Me_2-py	11.6	
MeCN, PhCN	14.1, 13 .8	
μ-OAc	< 3.2*	

Planas, N.; Maseras, F.; Sala, X.; Llobet, A. et al. *Chem. Eur. J.* **2010**, *1(3), 284.*



Flexible Molecule: Dynamic Behavior





C_2 symmetry

d(Ru-Ru) = 4.31 Å

d(O-O) = 2.23 Å

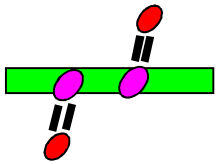
ΔG* small

Avoids Ru-O-Ru formation

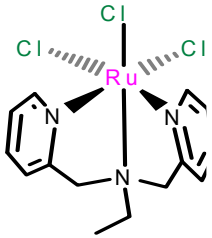
Favors intra-I2M O-O coupling

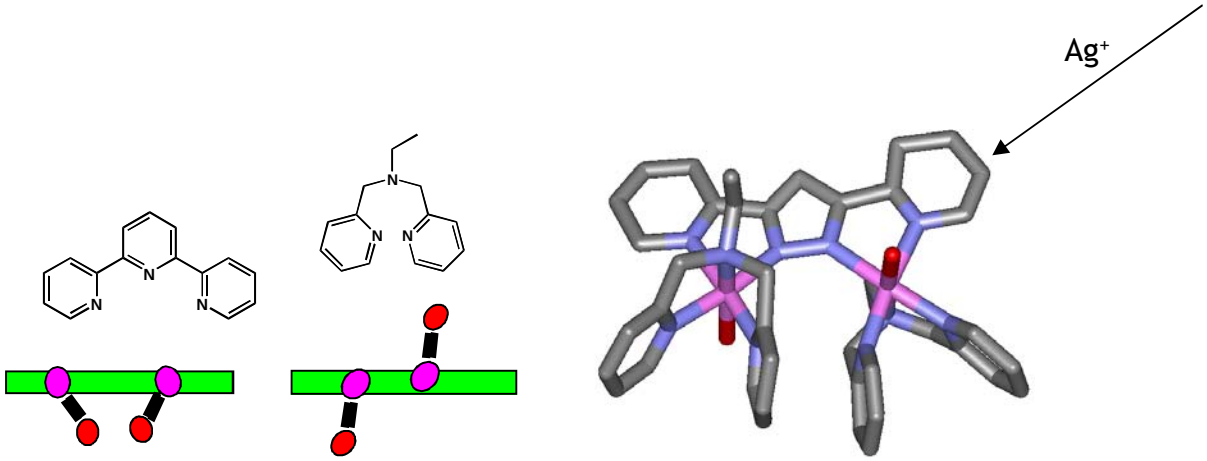
Planas, N.; Maseras, F.; Sala, X.; Llobet, A. et al. *Chem. Eur. J.* **2010**, *1(3), 284.*

HOMOGENEOUS WOC: Ru-Hbpp complexes: O-O bond formation



: *trans*- active sites – avoiding *the intramolecular pathway*

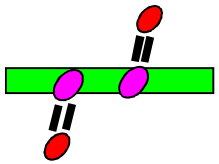




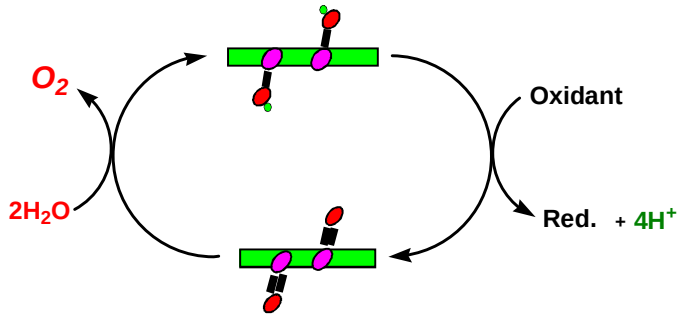
***up,down* - $(Ru^{III}\text{-}OH)_2$**

Mola, J, Sala, X. Llobet, A. *Dalton Trans.*, **2010**, 40, 3640

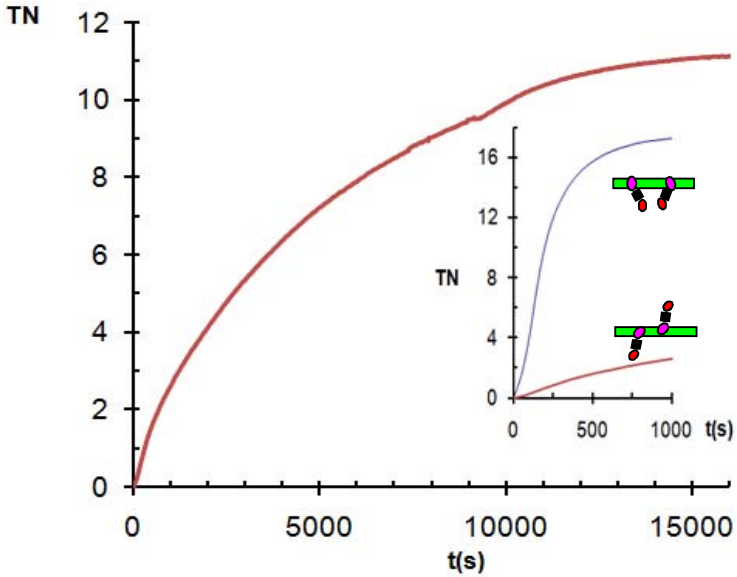
HOMOGENEOUS WOC: Ru-Hbpp complexes: O-O bond formation

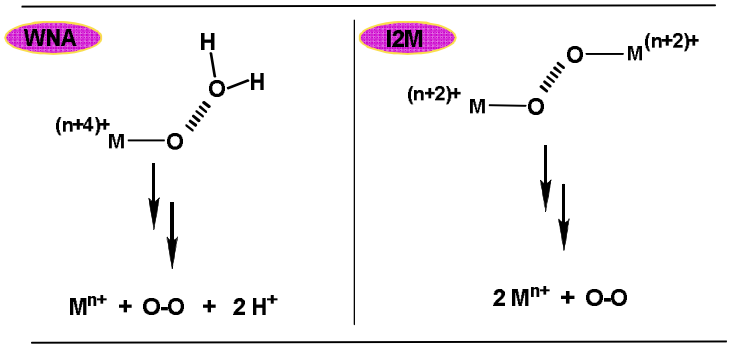


: *trans*- active sites – avoiding *the intramolecular pathway*



Ce(IV)





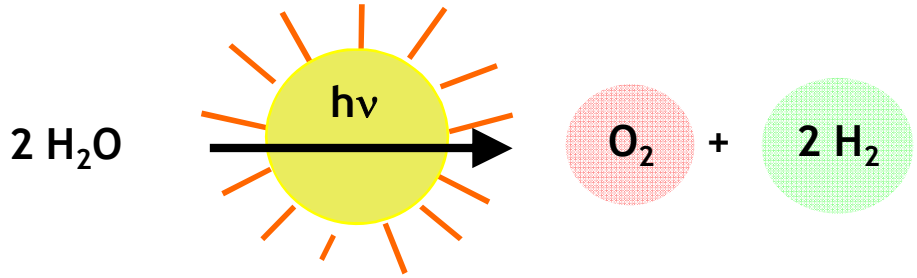
Mola, J, Sala, X. Llobet, A. *Dalton Trans.*, **2010**, 40, 3640

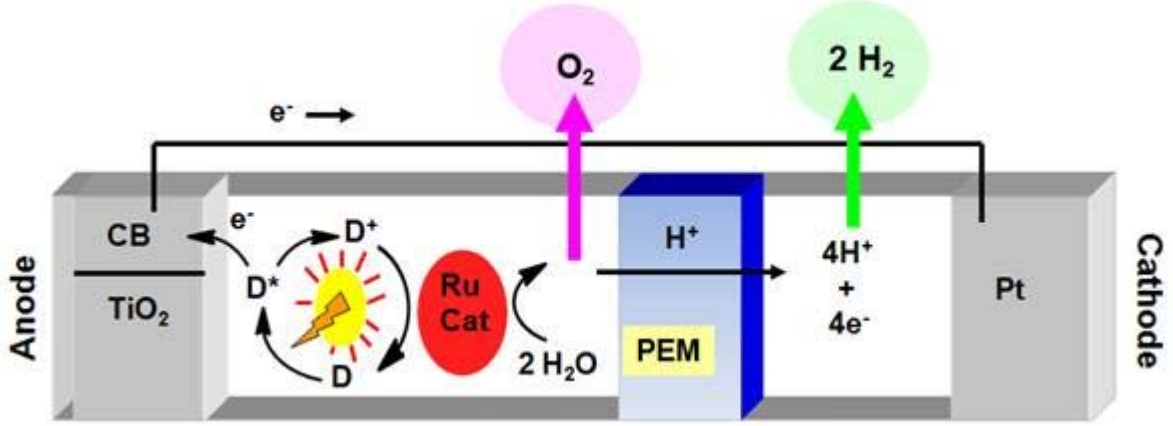
OUTLINE

Universitat Autònoma de Barcelona

1. INTRODUCTION
2. DINUCLEAR HOMOGENEOUS WOCs
3. DINUCLEAR HETEROGENEOUS WOCs
4. TETRANUCLEAR HOMOGENEOUS WOCs
5. MONONUCLEAR WOCs: the $[Ru(bpy)_2(H_2O)_2]$ case
6. CONCLUSIONS

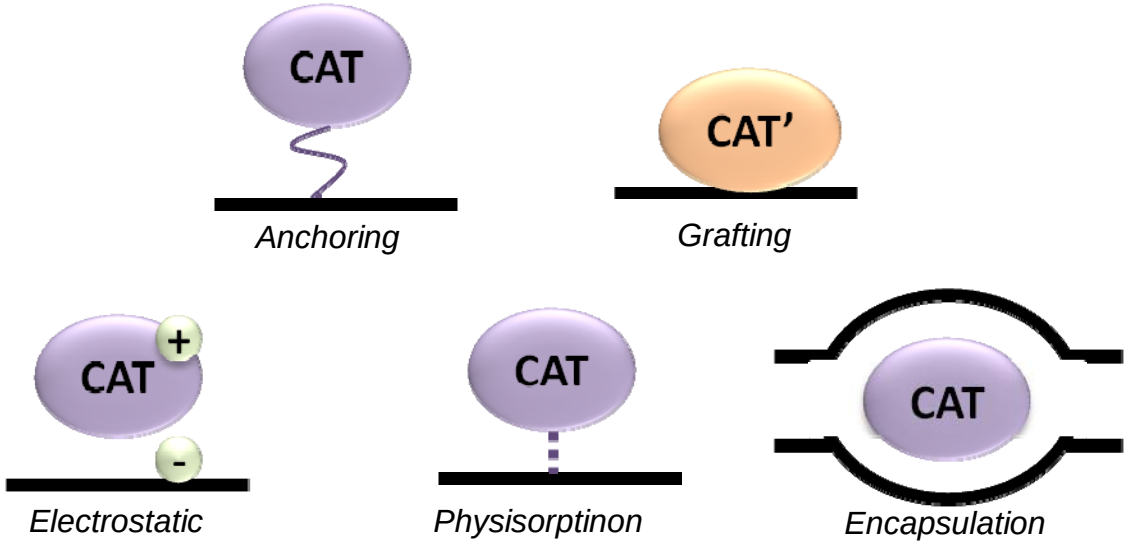
HETEROGENEOUS WOC: toward a PEC for H_2 production

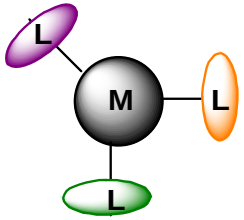




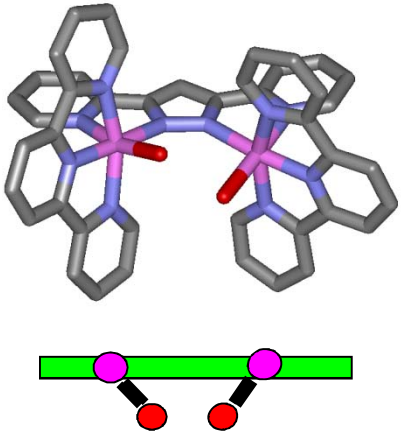
Sala, X.; Escriche, Ll.; Llobet, A. *Angew. Chem. Int. Ed.*, **2009,** 48, 2-13

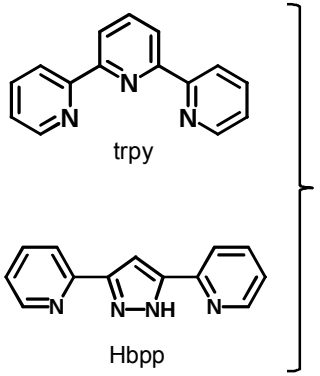
HETEROGENEOUS WOC: Immobilization strategies

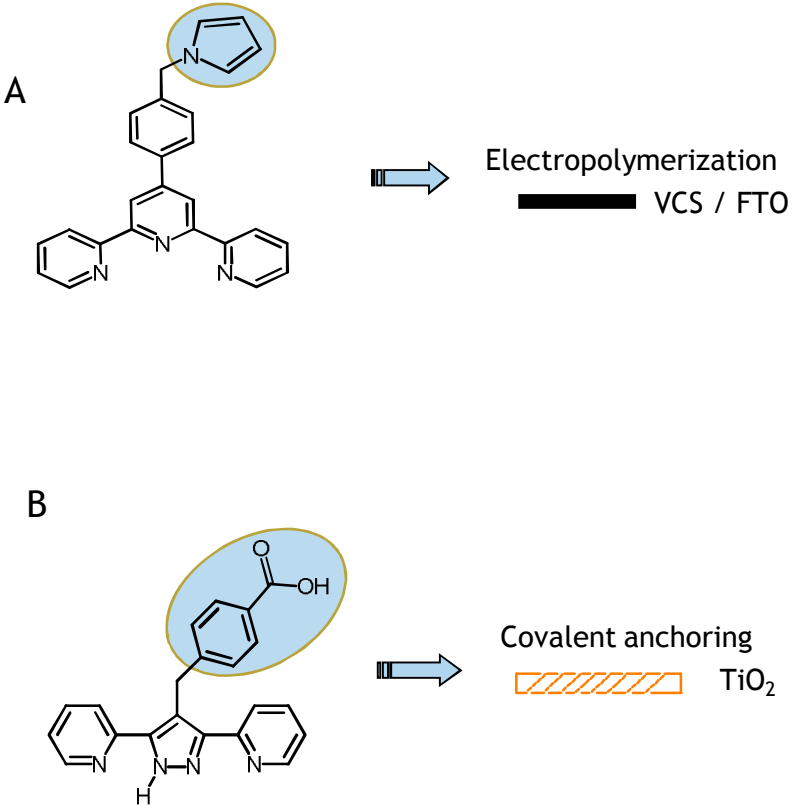




HETEROGENEOUS WOC: Ru-Hbpp complexes: Immobilization strategies

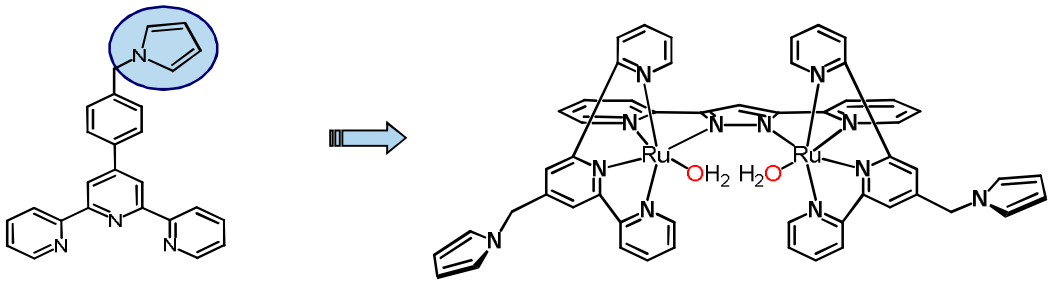


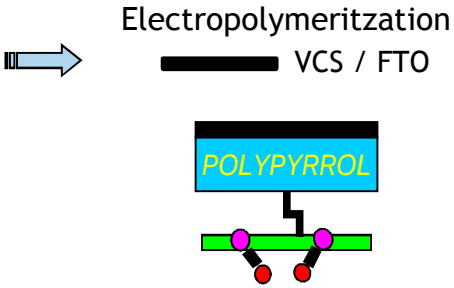


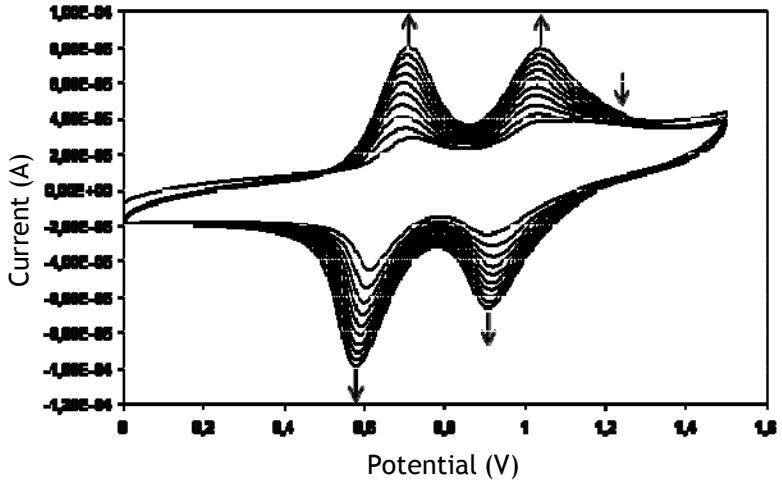


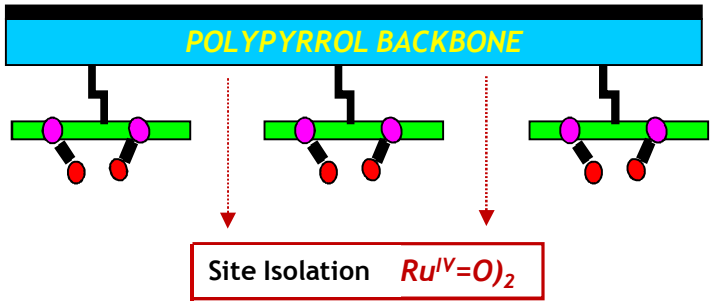
Ru-Hbpp complexes: immobilization - ELECTROPOLYMERIZATION

A





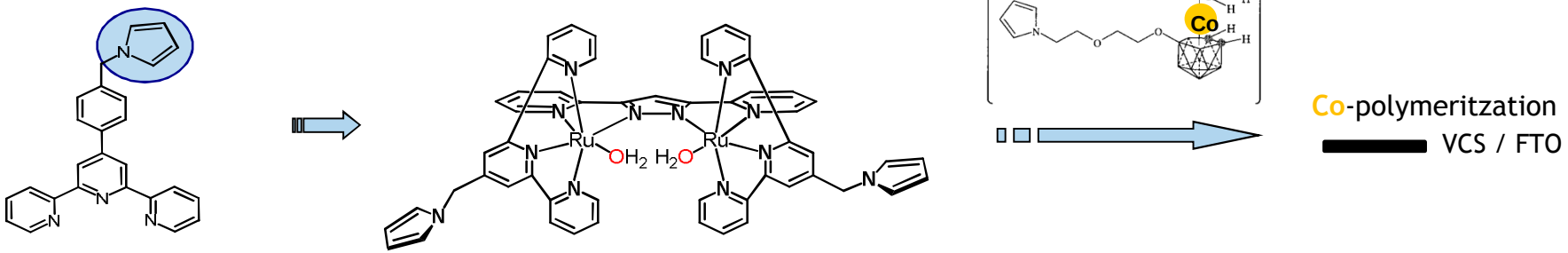


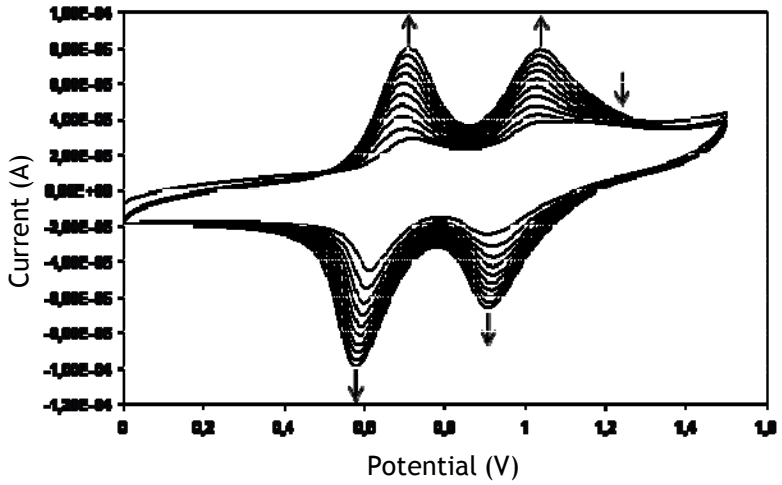


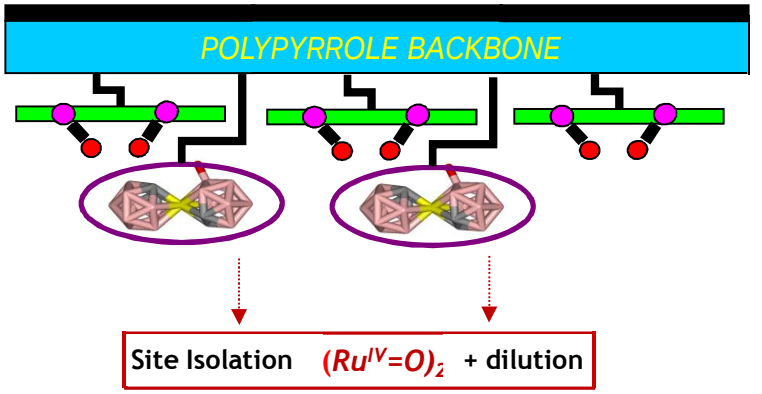
Angew. Chem. Int. Ed. **2008**, 47, 5830-5832

Ru-Hbpp complexes: immobilization - ELECTROPOLYMERIZATION

A

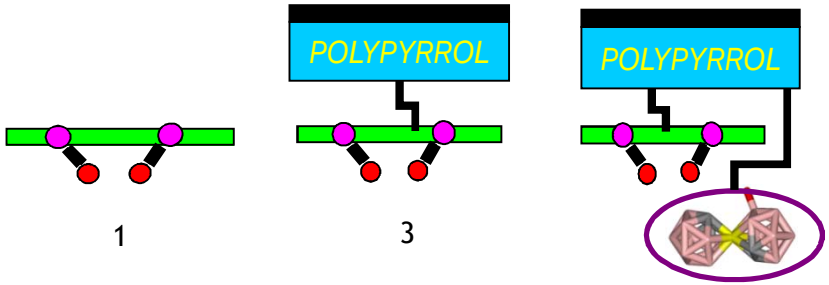




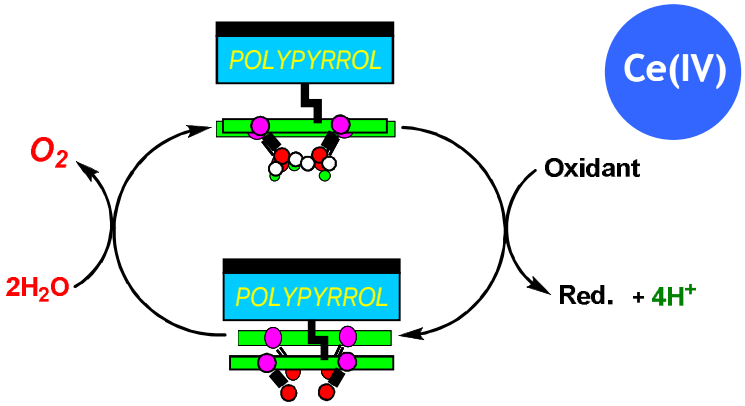


Angew. Chem. Int. Ed. **2008**, 47, 5830-5832

Ru-Hbpp complexes: immobilization - ELECTROPOLYMERIZATION



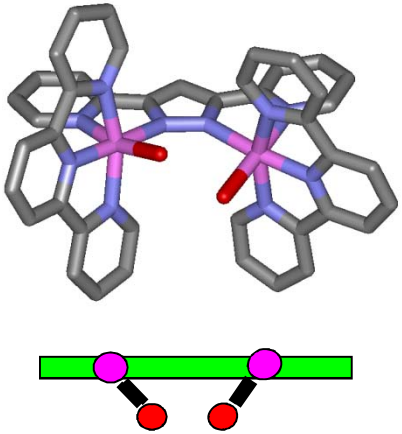
Cat	nmols Ru	mmols Ce(IV)	Ratio	TN	υ_{O2}x10^2
1	1828	186	102	18.6	2.5
1	167	857	5132	22.9	86
VCS/poly-**3**	3.1	3600	1162	41	0.62
FTO/poly-**3**	1.0	3600	3600	76	1.2
FTO/poly-(**3**-co-**4**)	0.5	3600	7200	**250**	1.1

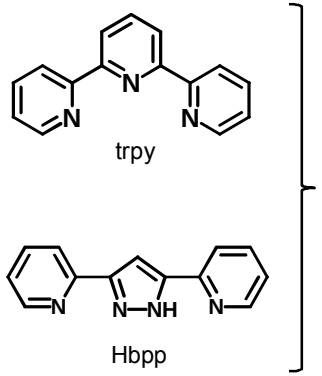


Max. TN reported in heteterogeneous phase with a chemical oxidant (Ce^{IV})

Angew. Chem. Int. Ed. **2008**, 47, 5830-5832

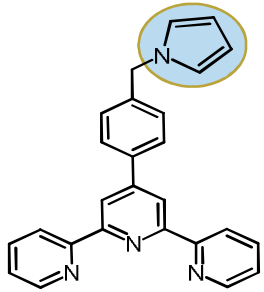
Ru-Hbpp complexes - IMMOBILIZATION STRATEGIES





Sens, C., Llobet, A., *J. Am. Chem. Soc.*, **2004**, 126, 7798

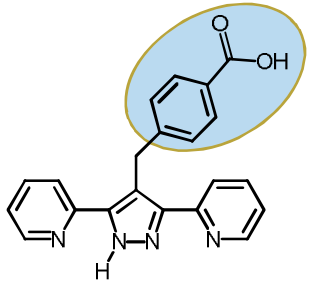
A



Electropolymerization

VCS / FTO

B



Covalent anchoring

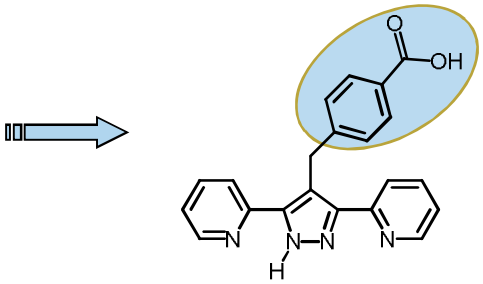
TiO_2

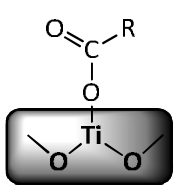
Ru-Hbpp complexes: immobilization - COVALENT ANCHORING

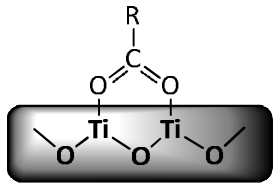
B

Covalent anchoring

TiO_2

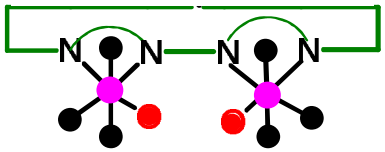






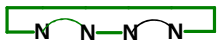
Solid Support = TiO_2

Lligand Modification

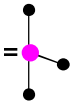


$[Ru_2(bpp)(trpy)_2(OH_2)]^{2+}$

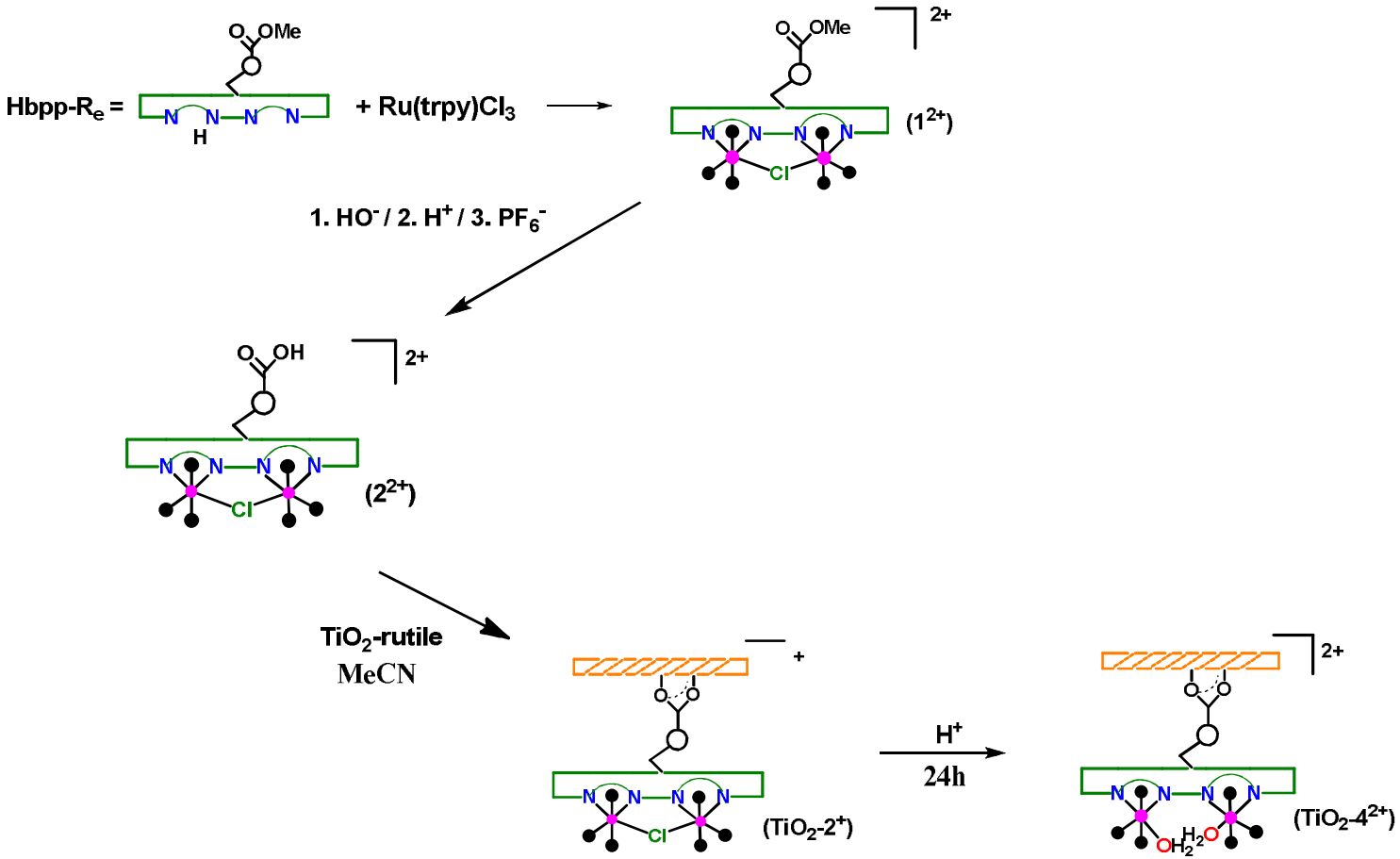
Hbpp =



Ru^{II}-trpy =



Ru-Hbpp complexes: anchoring strategies – COVALENT ANCHORING



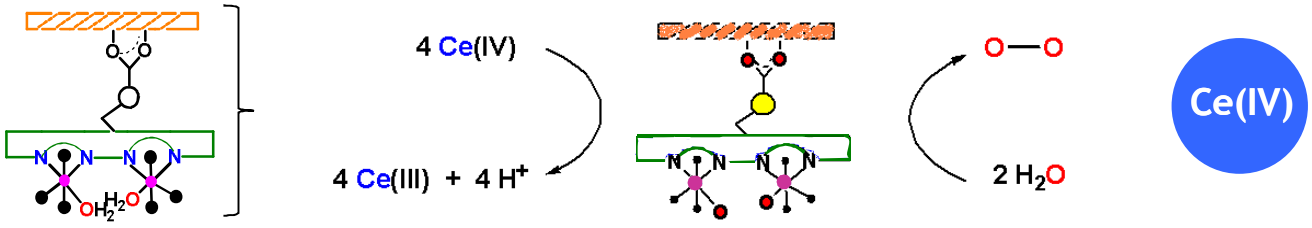
ChemSusChem **2009**, 2, 321-329

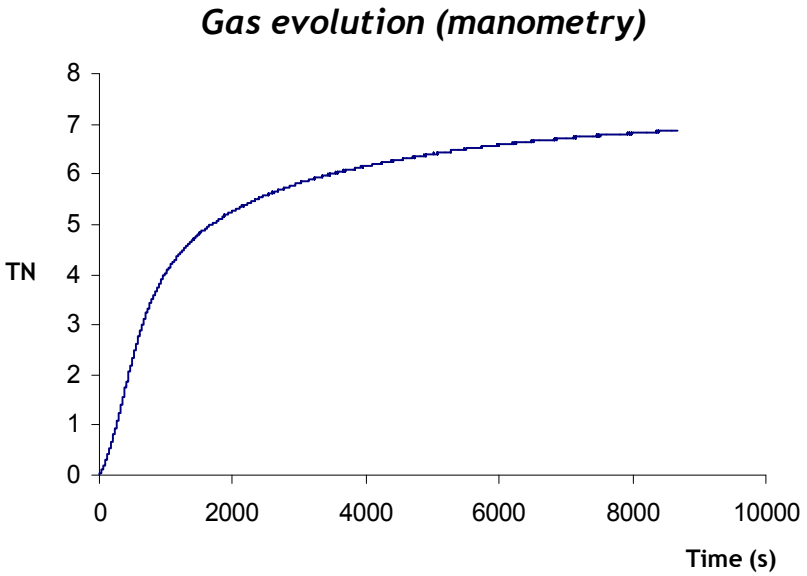
Hbpp-Re =

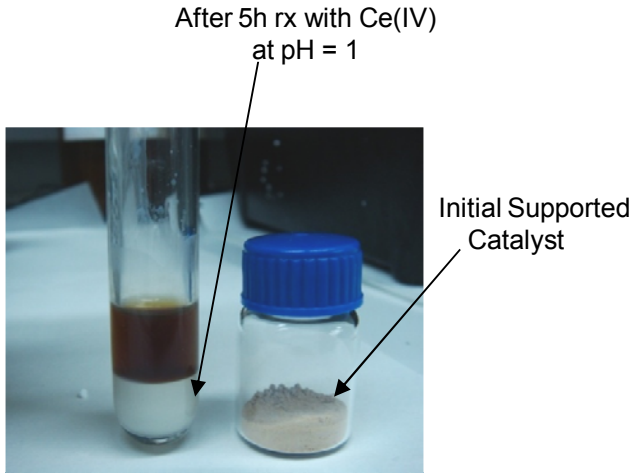
Ru^{II}-trpy =

TiO$_2$-rutile

Ru-Hbpp complexes: - Covalent anchoring - WATER OXIDATION



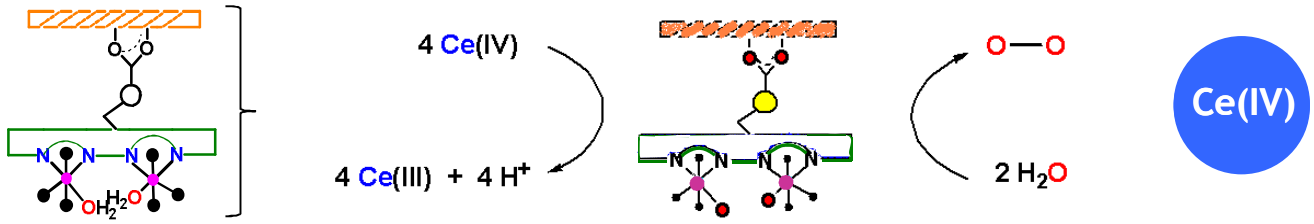


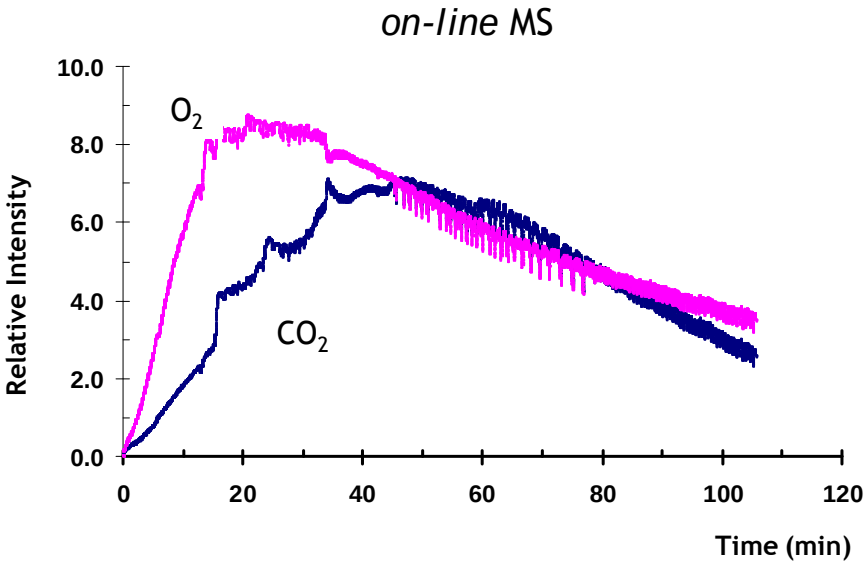


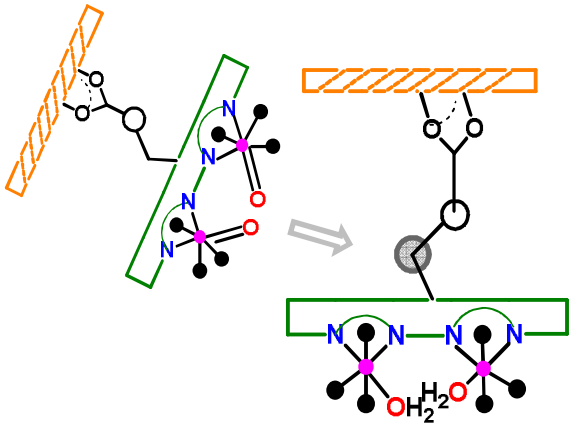
"Leaching" ⇨ CO_2 ?

ChemSusChem **2009**, 2, 321-329

Ru-Hbpp complexes: - Covalent anchoring - WATER OXIDATION







ChemSusChem **2009**, 2, 321-329

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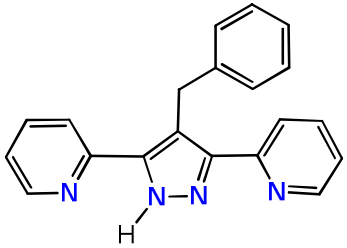
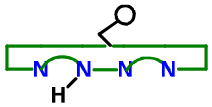
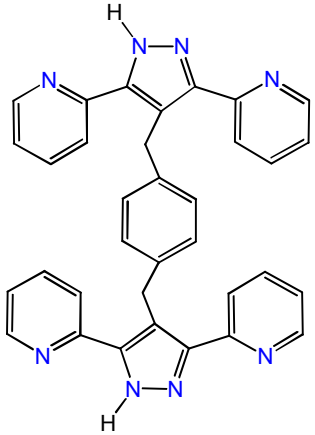
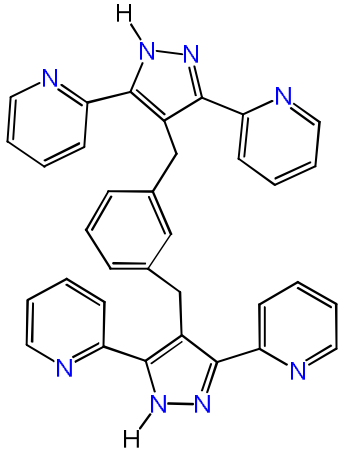
Ru-Hbpp complexes: - O_2/CO_2 vs. NUCLEARITY



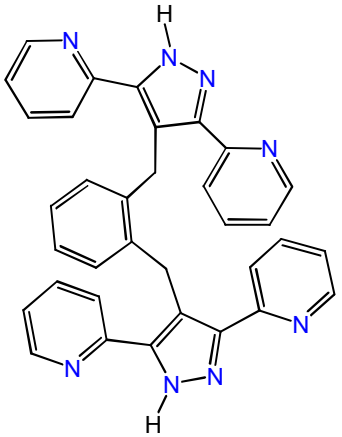
Hbpp-bz = 



$(Hbpp)_2pXyl$

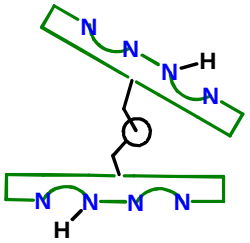


$(Hbpp)_2mXyl$



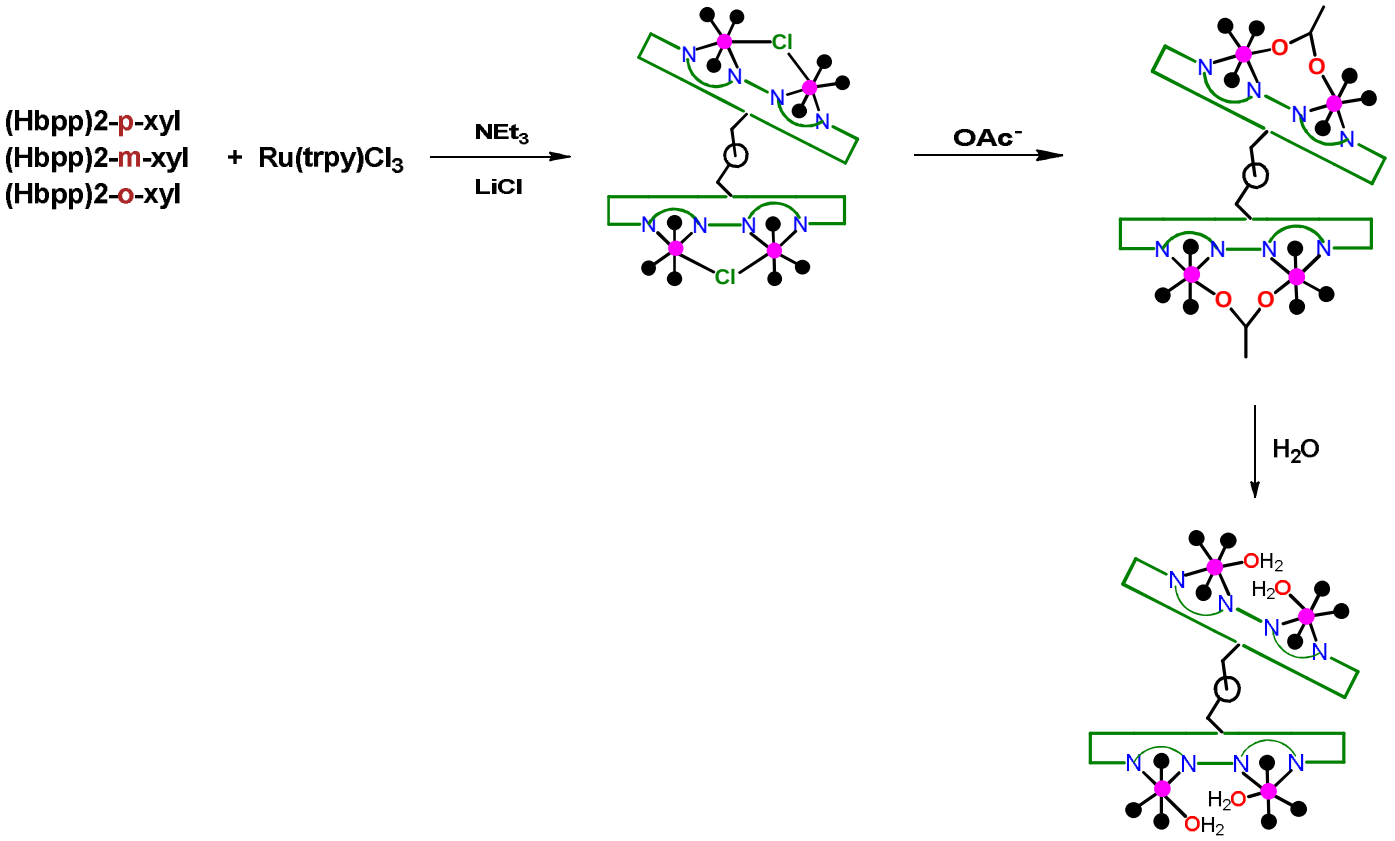
$(Hbpp)_2oXyl$

=

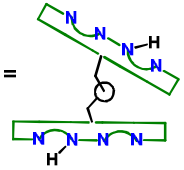


Francàs, L.; Sala, X.; Escriche, L.; Llobet, A. *Inorg. Chem* **2011**, 57, 2771

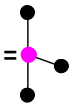
Ru-Hbpp complexes: - O_2/CO_2 vs. NUCLEARITY



(Hbpp)$_2$-*p*-xyl
(Hbpp)$_2$-*m*-xyl
(Hbpp)$_2$-*o*-xyl =



Ru^{II}-trpy =



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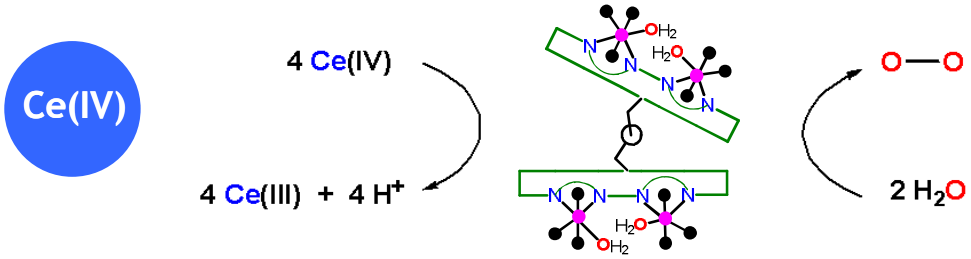
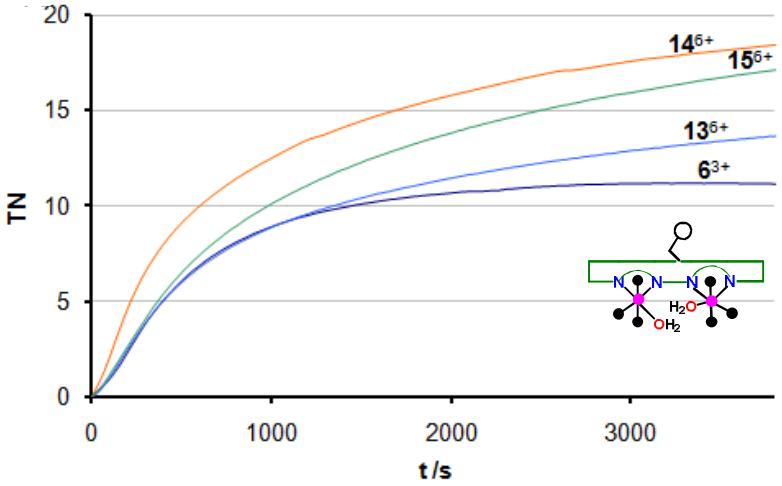
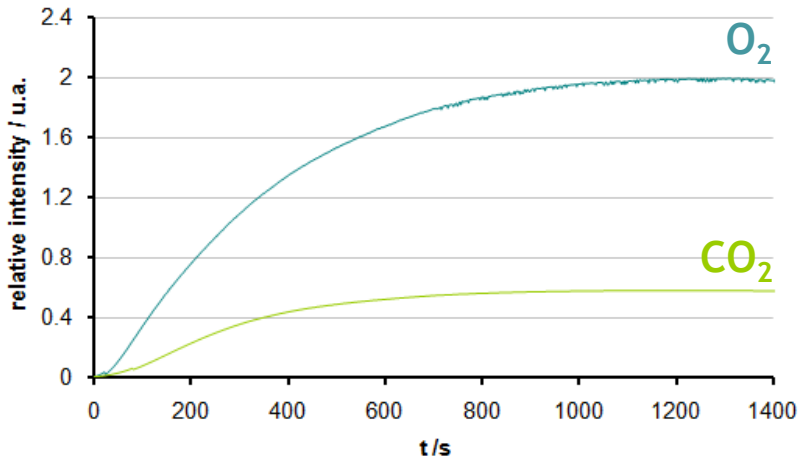


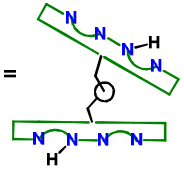
Catalytic gas generation (manometry)



On line MS profile



(Hbpp)$_2$-*p*-xyl
(Hbpp)$_2$-*m*-xyl
(Hbpp)$_2$-*o*-xyl



Ru^{II}-trpy =

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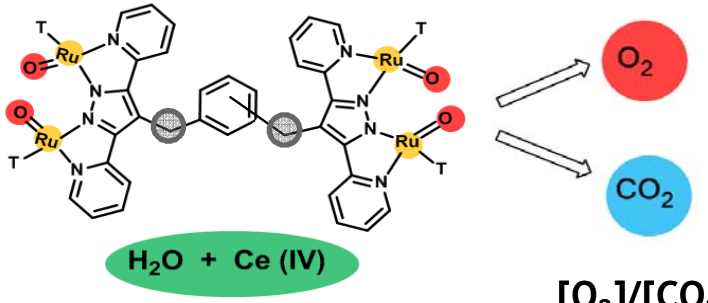
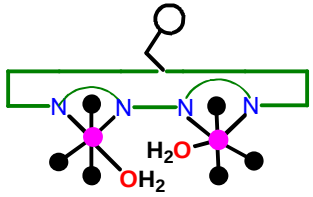
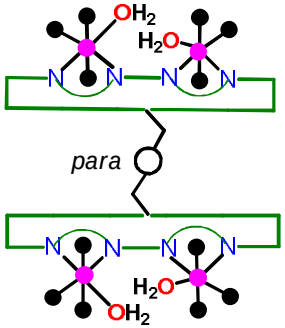
Ru-Hbpp complexes: - O_2/CO_2 vs. NUCLEARITY



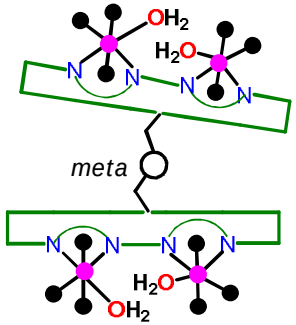
$[O_2]/[CO_2]$



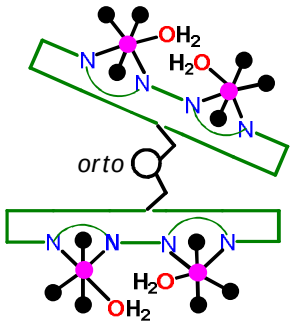
1.0



2.1 | 2.5

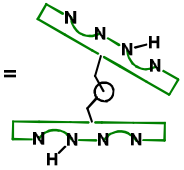


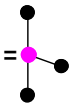
2.0 | 2.5



2.0 | 3.0

[CAT]=0.5mM, Ce/Ru=50 | [CAT]=1mM, Ce/Ru=50

$(Hbpp)_2$-*p*-xyl
$(Hbpp)_2$-*m*-xyl = 
$(Hbpp)_2$-*o*-xyl

Ru^{II}-trpy = 

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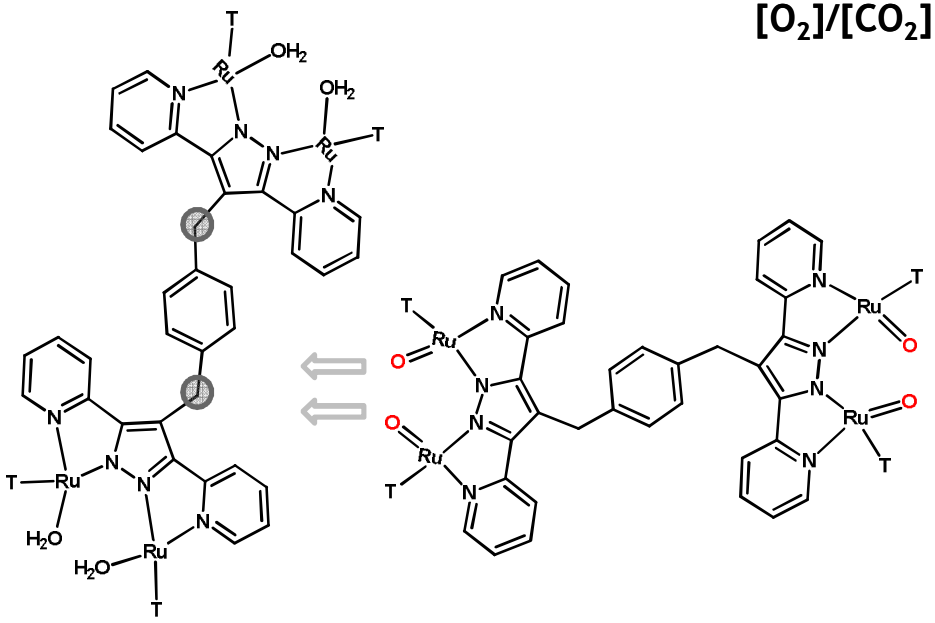
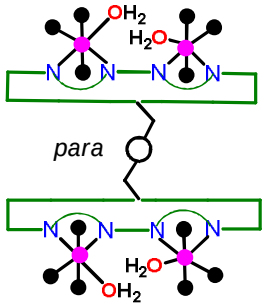
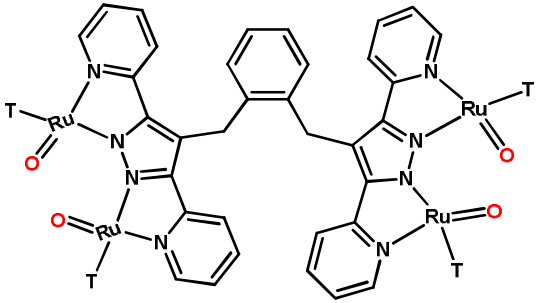
Ru-Hbpp complexes: - O_2/CO_2 vs. NUCLEARITY

$[O_2]/[CO_2]$

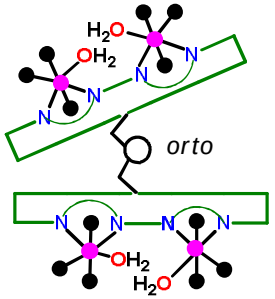


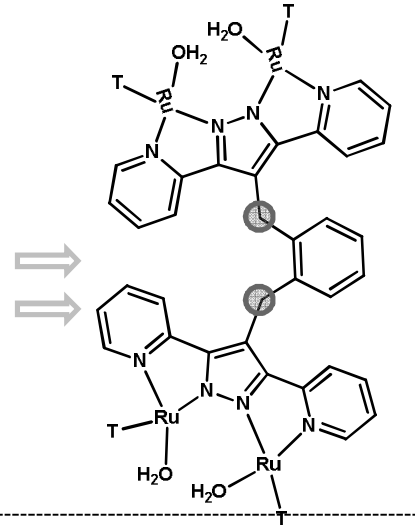


2.5

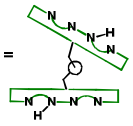


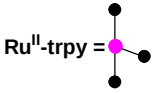
3.0





(Hbpp)$_2$-*p*-xyl
(Hbpp)$_2$-*m*-xyl =
(Hbpp)$_2$-*o*-xyl



Ru^{II}-trpy = 

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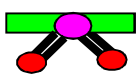
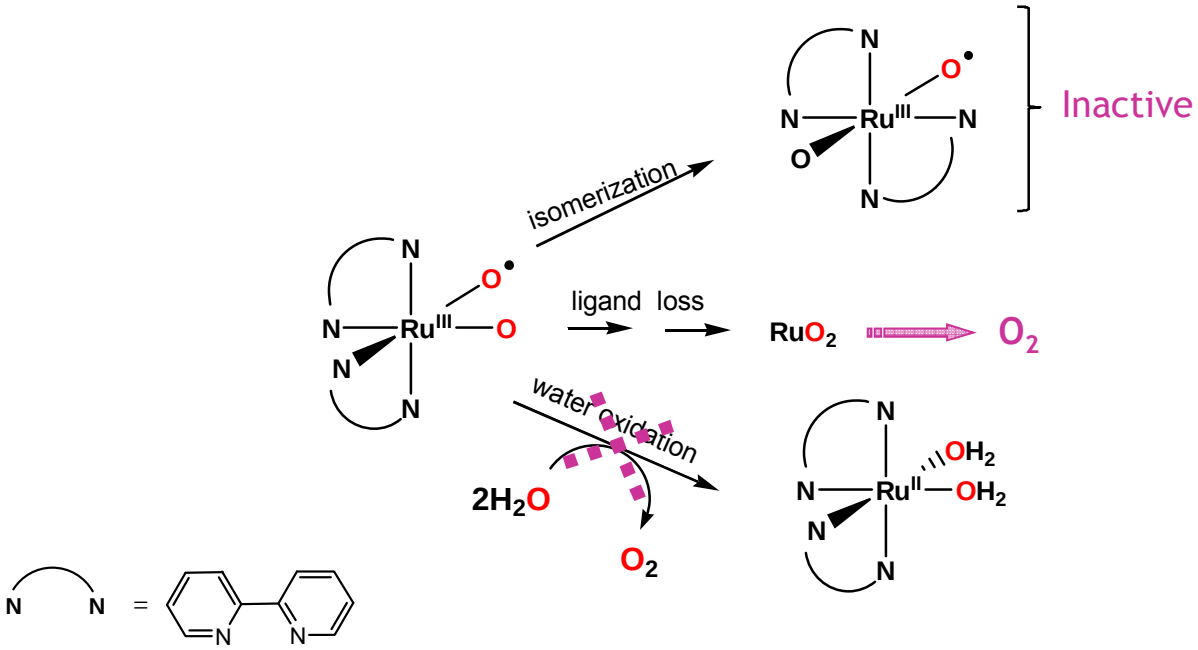
HOMOGENEOUS WOC: Ru-Hbpp complexes: O-O bond formation

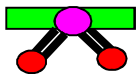


: *cis*-[Ru(bpy)(OH_2)]$^{2+}$, 20 years after – *O_2–generation mechanism*

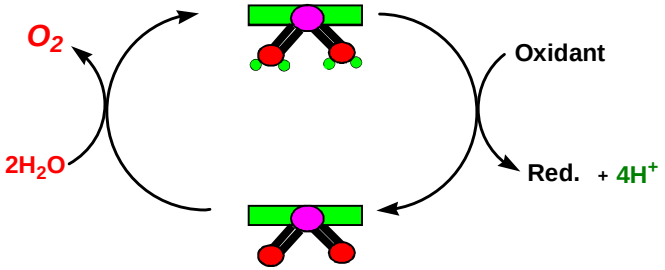


Dobson, J. C.; Meyer, T. J. Inorg. Chem., **1988**, 27, 3283

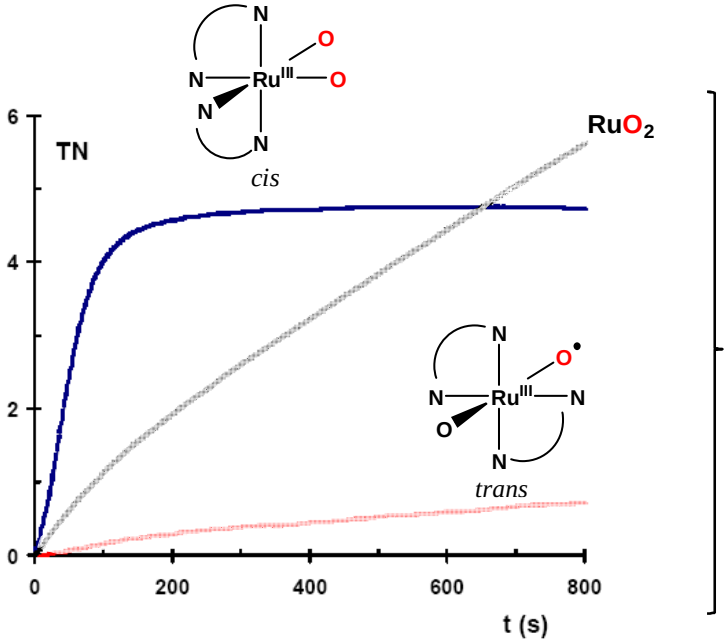
HOMOGENEOUS WOC: Ru-Hbpp complexes: O-O bond formation

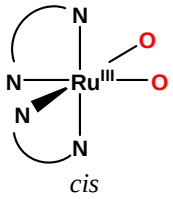


: *cis*-[Ru(bpy)(OH_2)]$^{2+}$, 20 years after – *O_2–generation mechanism*



Ce(IV)



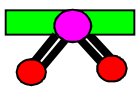


Active as WOC

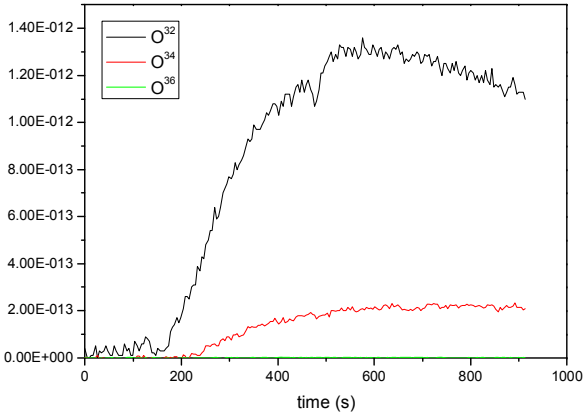
- Interesting for studying the O-O bond formation pathways

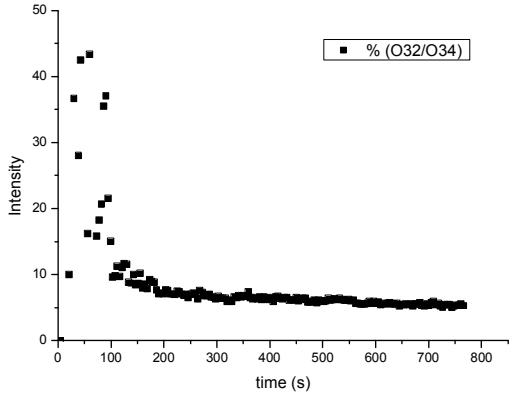
Sala, X.; Cramer, C.; Gagliardi, L.; Llobet, A. et al. Angew. Chem. Int. Ed. **2010**, 49, 7745-7747

HOMOGENEOUS WOC: Ru-Hbpp complexes: O-O bond formation



: *O_2-generation mechanism* – cat O^{16} /O^{18} and solvent H_2O^{16}/H_2O^{18}

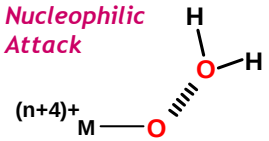




Entry	O^{18} (%)	Exchange		NucA-T	IntraM-T	Exp.
4	Cat, 19.4 Solv, 9.7	$^{32}O_2$	81.50	72.80	65.5	73.3
5		$^{34}O_2$	17.50	25.30	31.3	25.40
6		$^{36}O_2$	0.9	1.90	3.8	1.3

1st direct evidence of a

100% WNA for **O-O bond formation**



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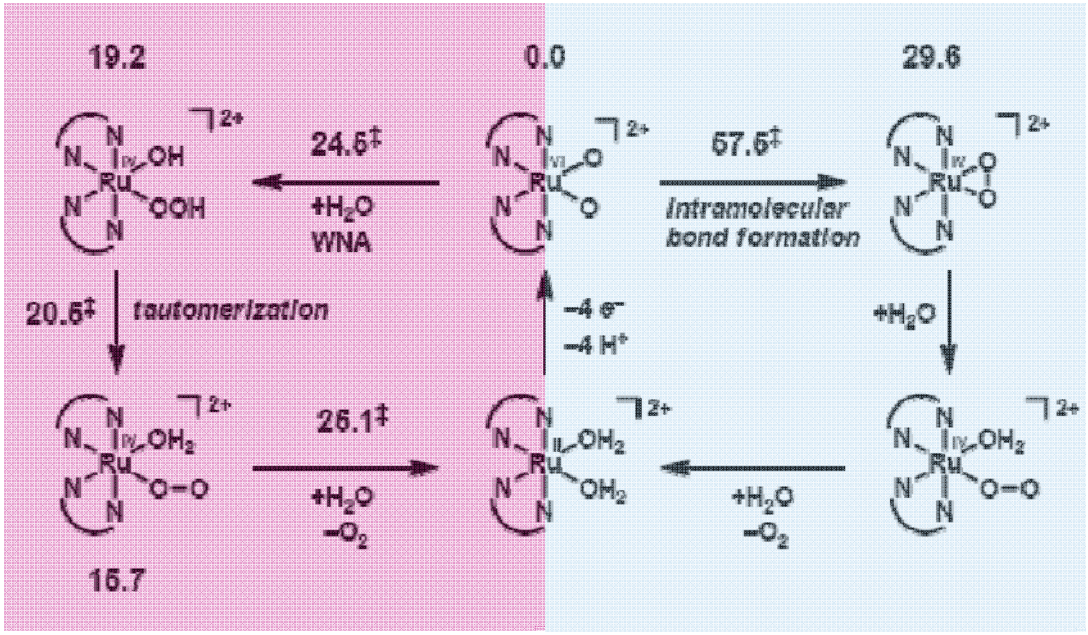
HOMOGENEOUS WOC: Ru-Hbpp complexes: O-O bond formation

: *O_2-generation mechanism – theoretical work*

Nucleophilic Attack (WNA)



Intra-molecular

Favoured by **32.4 Kcal/mol**

Sala, X.; Cramer, C.; Gagliardi, L.; Llobet, A. et al. Angew. Chem. Int. Ed. **2010**, 49, 7745-7747

OUTLINE

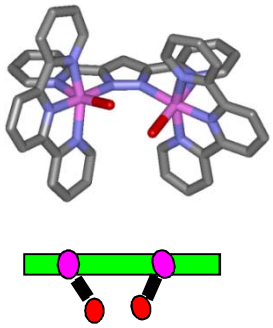
Universitat Autònoma de Barcelona

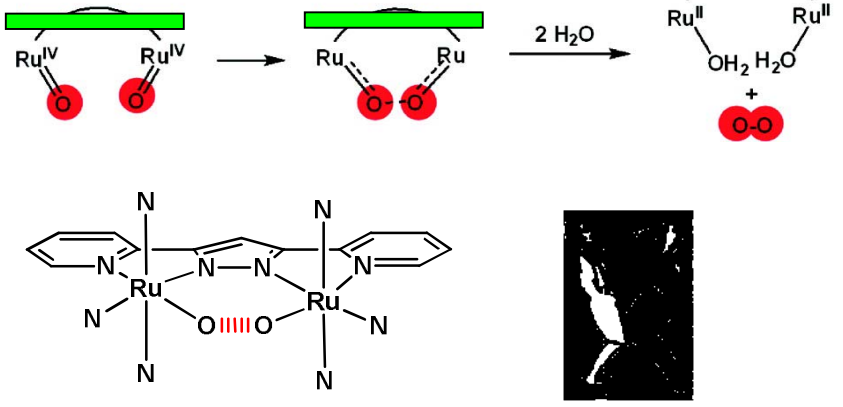
1. INTRODUCTION
2. DINUCLEAR HOMOGENEOUS WOCs
3. DINUCLEAR HETEROGENEOUS WOCs
4. TETRANUCLEAR HOMOGENEOUS WOCs
5. MONONUCLEAR WOCs: the $[Ru(bpy)_2(H_2O)_2]$ case
6. CONCLUSIONS

CONCLUSIONS

Ru-Hbpp Homogeneous WOCs

1

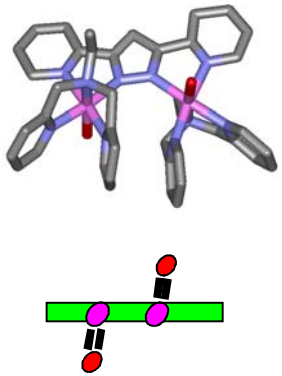


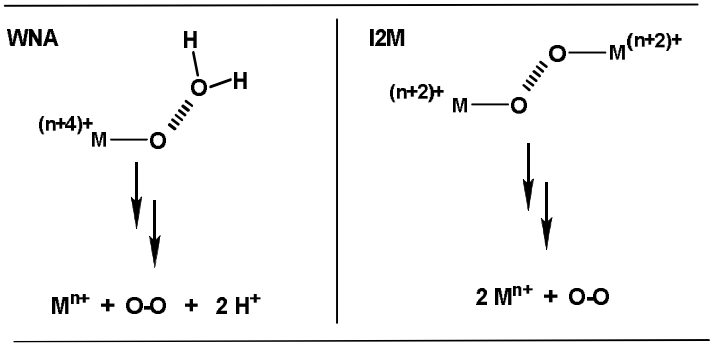


100 % INTRA-molecular

Dynamic Behaviour

2



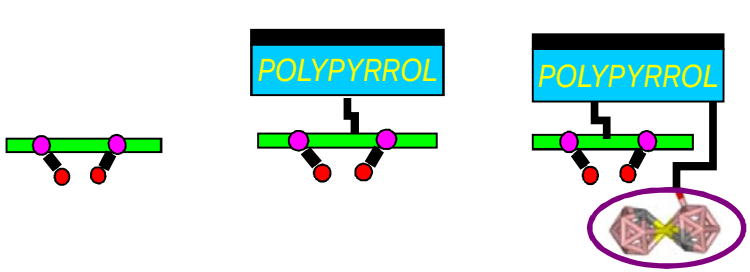


INTERM-IM2 or WNA

CONCLUSIONS

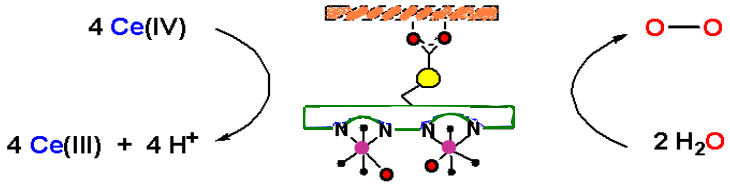
Ru-Hbpp Heterogeneous WOCs

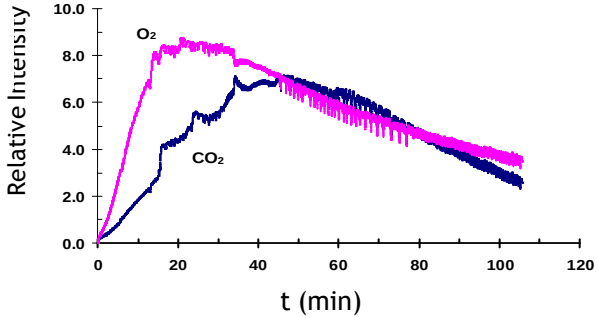
3 **Electropolymerization (VCS / FTO)**



- Cat-Cat oxidative deactivation
- Site isolation + Dilution
- Polymeric matrix oxidation

4 **Covalent anchoring (TiO_2)**

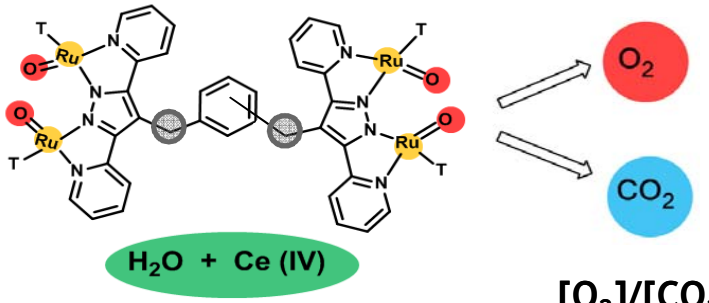




CONCLUSIONS

Tetranuclear WOCs

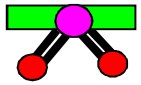
5 **O_2/CO_2 ratio**

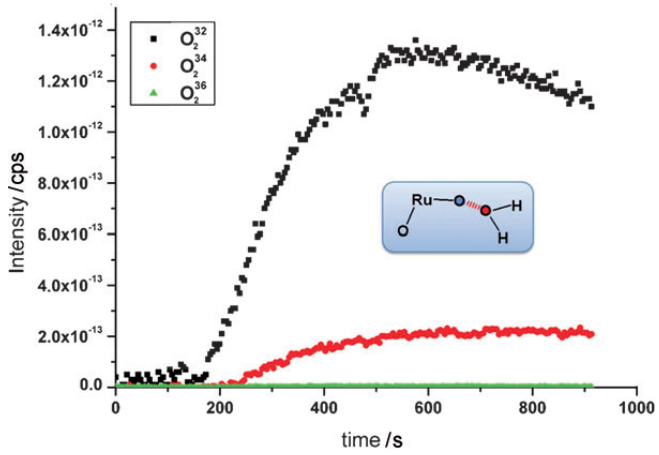


$[O_2]/[CO_2]$

Mononuclear WOCs

6 **The $[Ru(bpy)_2(H_2O)_2]$ case : O_2 formation**





100% WNA

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Ru Based Water Oxidation Catalysts

ICTP, Miramare, Trieste, October 19th 2011

Xavier Sala, UAB, Barcelona, Spain