ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

2023 PhD Week

Energy and Environmental Engineering Sciences

18/10/2023

MOLECULAR APPROACHES TO SUSTAINABLE CATALYSIS

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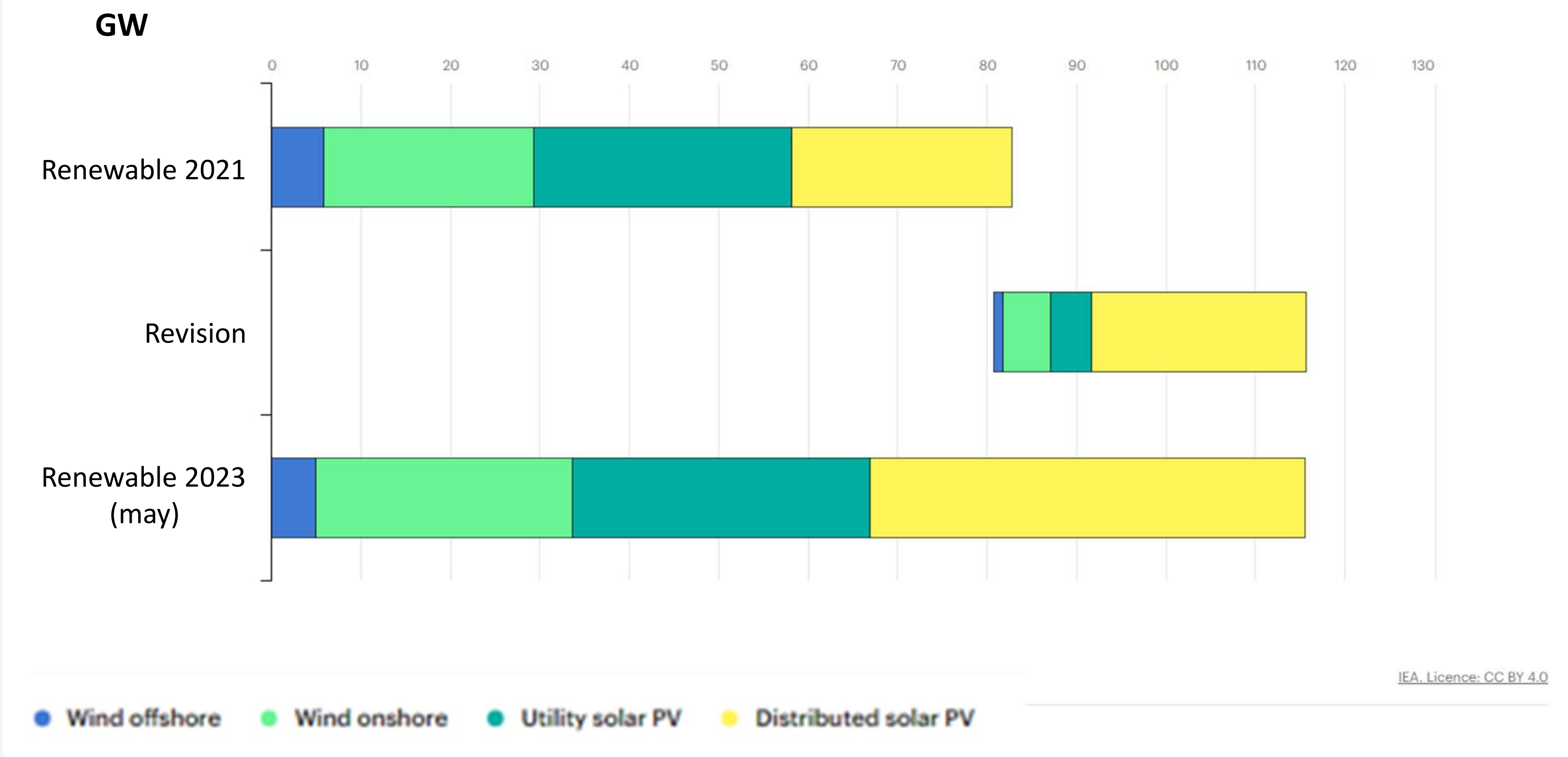
Department of Industrial Chemistry «Toso Montanari»

Sustainability 2030 Agenda: Where do we need to (rapidly) go?

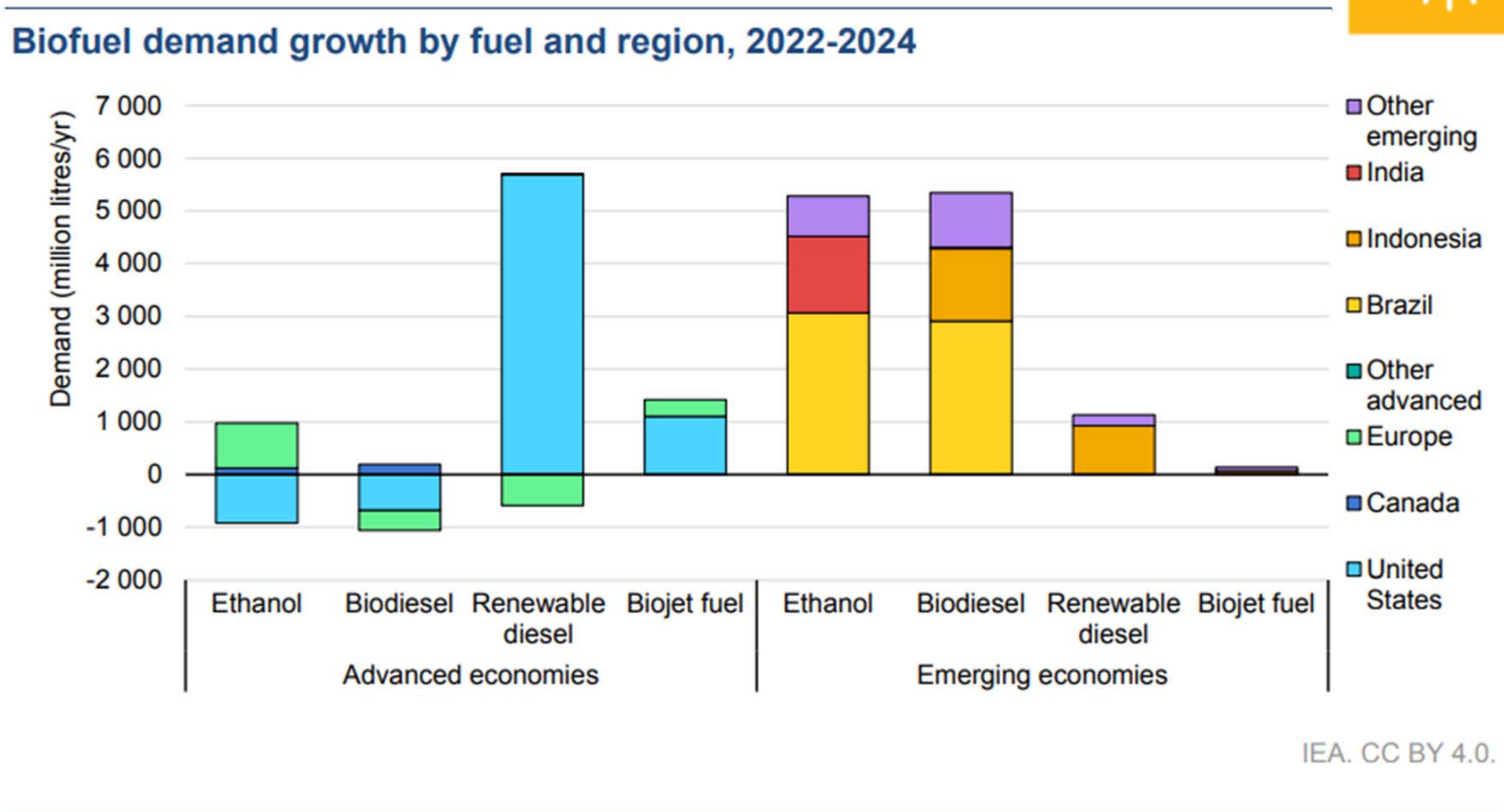
Renewable Energy Market Update: outlook for 2023 and 2024



Appears in
[Renewable Energy Market Update - June 2023](https://www.iea.org/data-and-statistics/charts/european-union-capacity-additions-in-2023-2024)

https://www.iea.org/data-and-statistics/charts/european-union-capacity-additions-in-2023-2024

Renewable Energy Market Update: outlook for 2023 and 2024

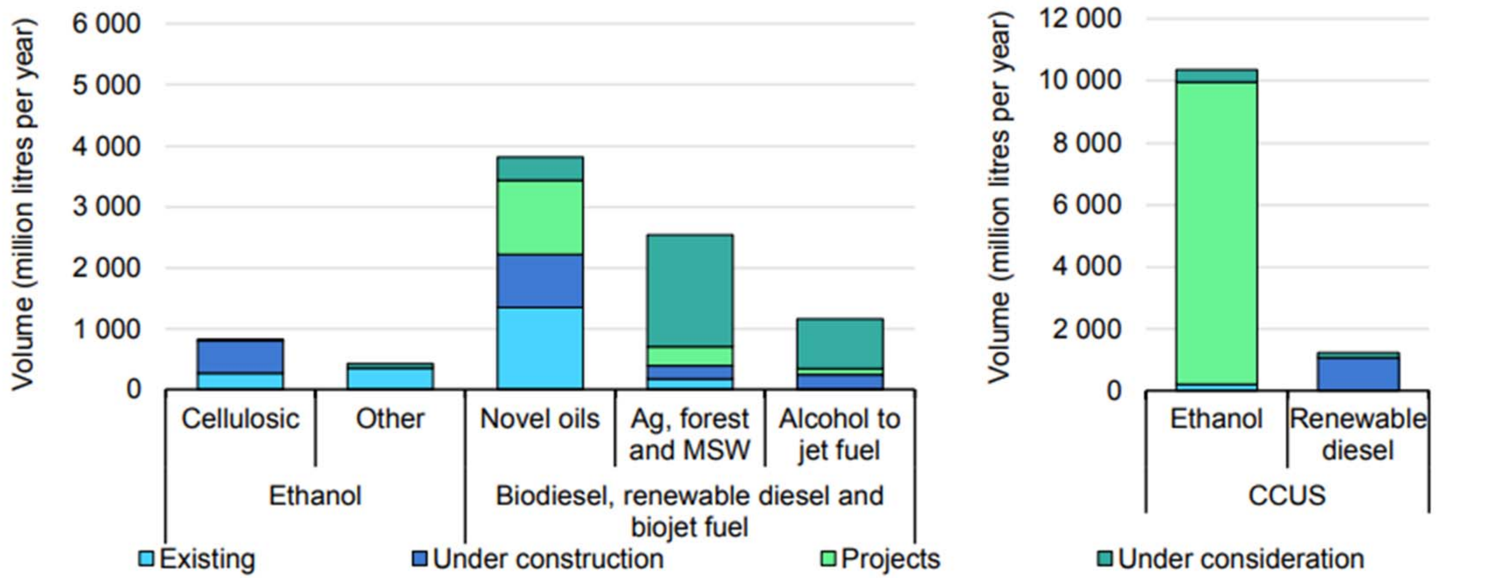


- EU Renewable Energy Directive (REDIII), aims to achieve 14% renewable transport fuels by 2030

IEA, European Union capacity additions in 2023-2024, IEA, Paris https://www.iea.org/data-and-statistics/charts/european-union-capacity-additions-in-2023-2024, IEA. Licence: CC BY 4.0

The shadow of feedstock supply crunch

Existing and planned biofuel capacity using non-conventional feedstocks and incorporating CCUS, 2021-2030

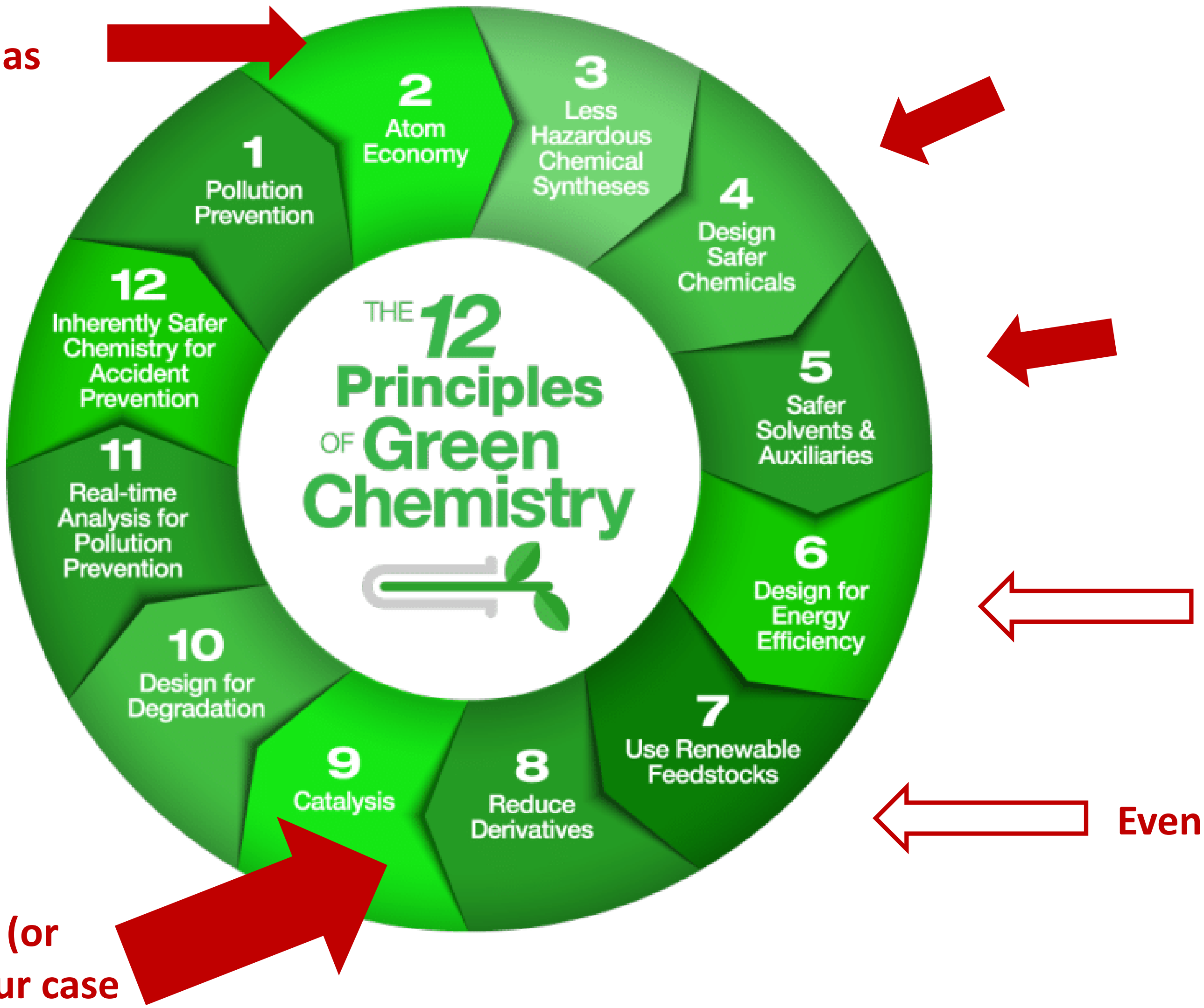


Notes: CCUS = carbon capture, utilisation and storage. MSW = municipal solid waste. “Existing” projects are those with operational capacity as of the end of 2022. “Under construction” are projects being built as of Q1-2023. “Projects” are those with announced final investment decisions or otherwise highly likely to move forward as of Q1-2023. “Under consideration” covers all other announced projects with planned operation dates as of Q1-2023.

What do we need to (re-)use as feedstocks?

Let’s move to the «molecular» side of the moon: the twelve sustainable rules for chemists

Waste of the process: null or as low as possible



Even better if waste

Homogeneous (or «molecular») in our case

What's app in the industrial world of homogeneous catalysis?

Post

Johnson Matthey
@Johnson_Matthey

JM's investment in homogeneous ester hydrogenation allows us to provide our customers with enhanced safety, simplicity, and sustainability of their synthetic routes.

Johnson Matthey
163.293 follower
2 giorni · Modificato

❓ Did you know ❓ In 2030, 30 billion litres of sustainable aviation fuel (#SAF) will need to be produced to stay in line with global net zero projections? 🌍 ✈️

🧠 Hear from our SAF expert Paul Ticehurst, Senior Business Development Director, as he delves into some of the ways governments can stimulate further growth for SAF 📈

Find the article here: https://bit.ly/3LzRmpl

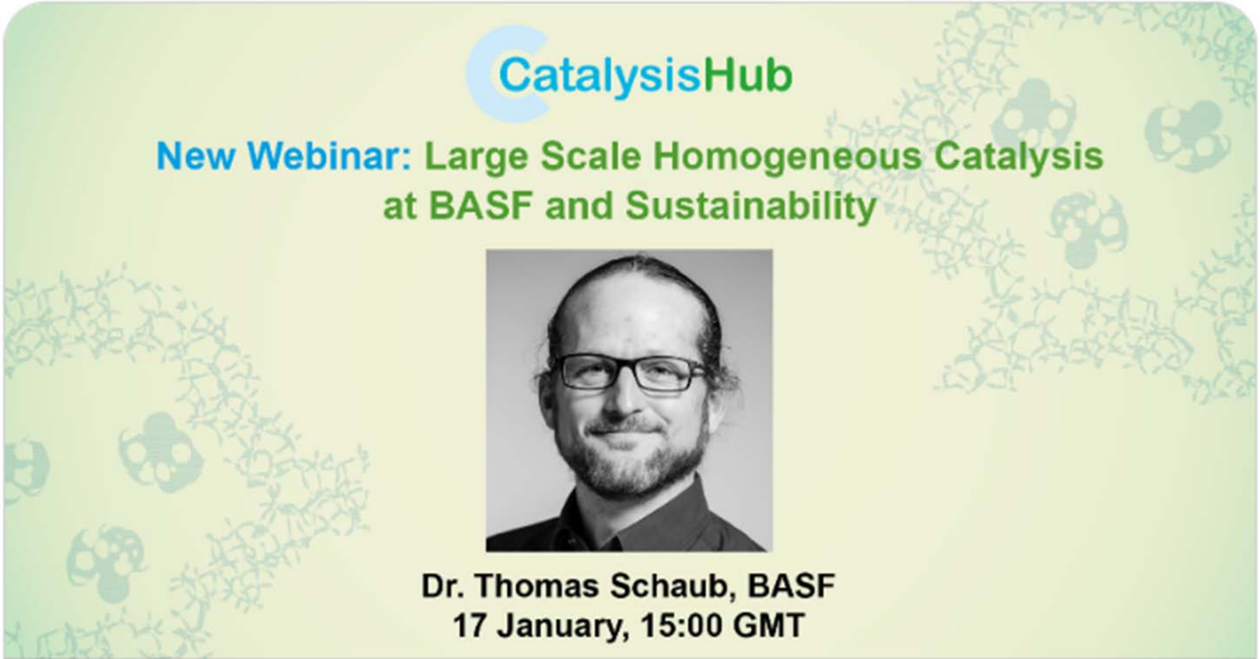
#SustainableAviation #CatalysingNetZero

This is actually still in the heterogeneous world of catalysis, but it is a very interesting trend anyway

facebook RSC Applied Catalysis Group

What's app in the industrial world of homogeneous catalysis?

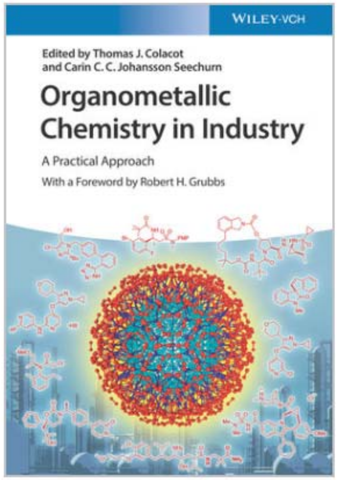
New webinar on homogeneous catalysis coming up



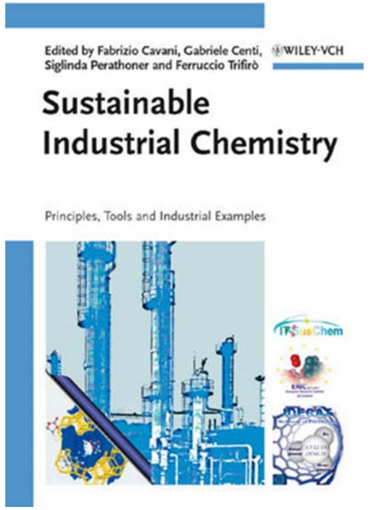
UK Catalysis Hub
9 dicembre 2022 ·

We have a new webinar coming up on the 17th January 2023 on Large Scale Homogeneous Catalysis at BASF and Sustainability with Dr. Thomas Schaub. For Dr. Thomas ... **Altro...**

Molecular catalysis become convenient when selectivity is compulsory



- ***Heterogeneous*** catalysts dominate chemical and petrochemical industry: ~ 95% of all chemical processes use ***heterogenous*** catalysts.
- ***Homogenous catalysts*** are used when ***selectivity*** is critical and product-catalyst ***separation problems*** can be solved.



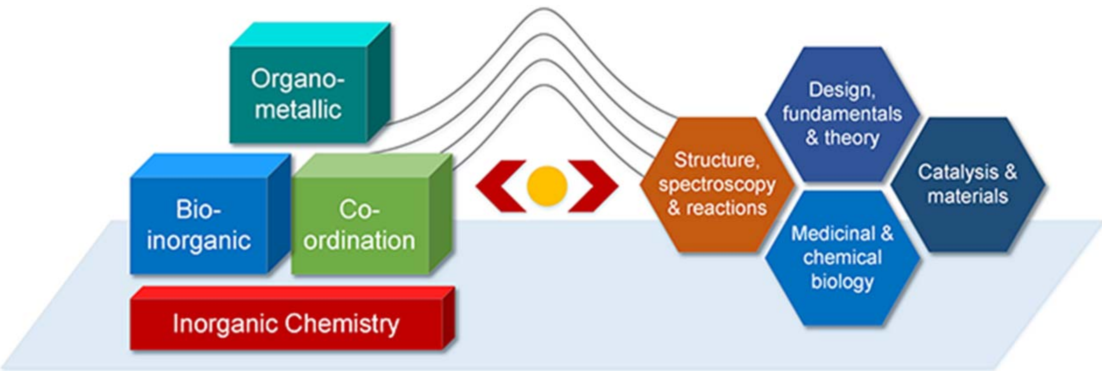
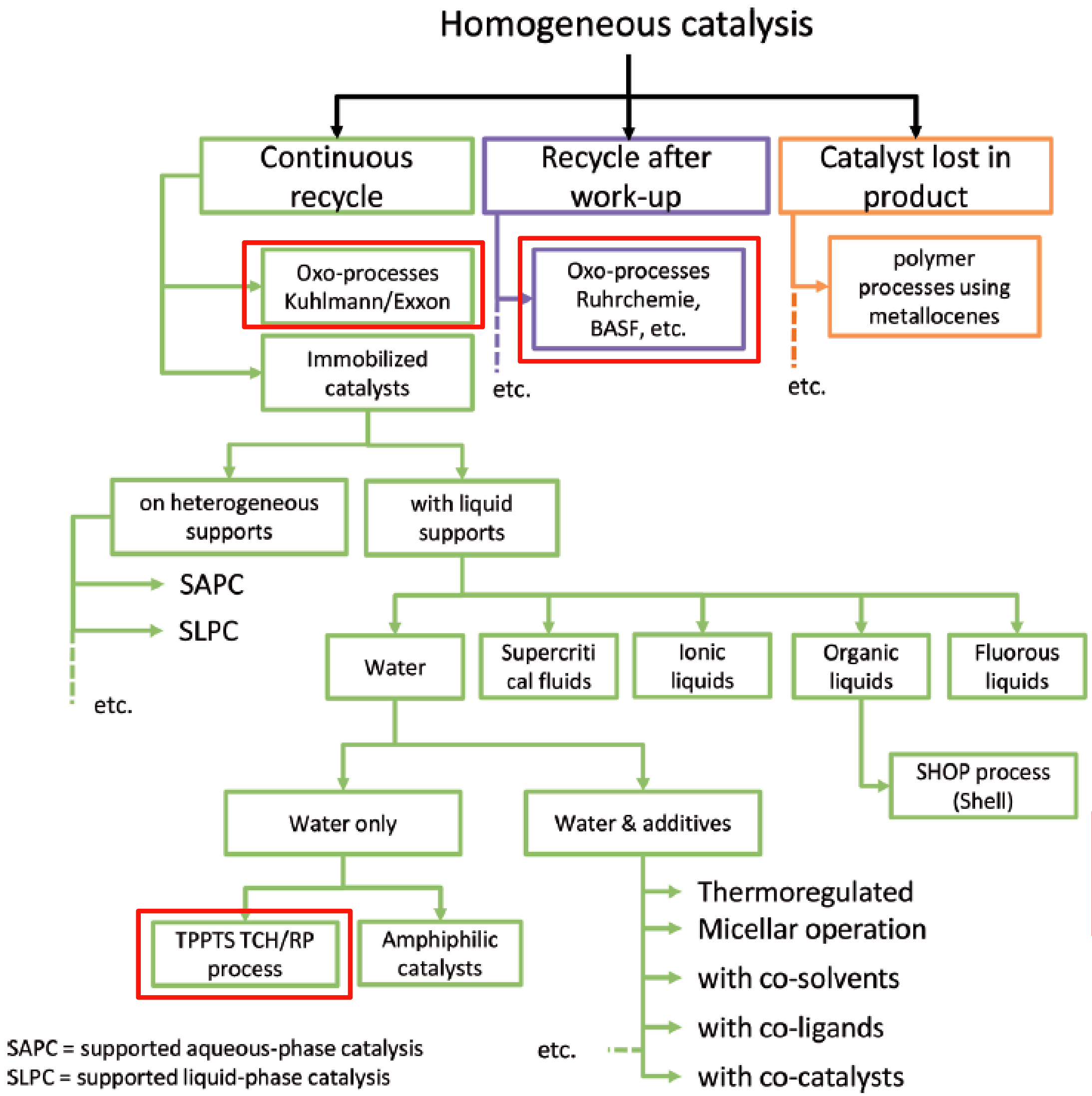


Figure 1.2 Vision of the F^3-Factory (future, fast, flexible).
Source: elaborated by ETP SusChem (http://www.suschem.org).

Homogeneous catalysis recycling modes

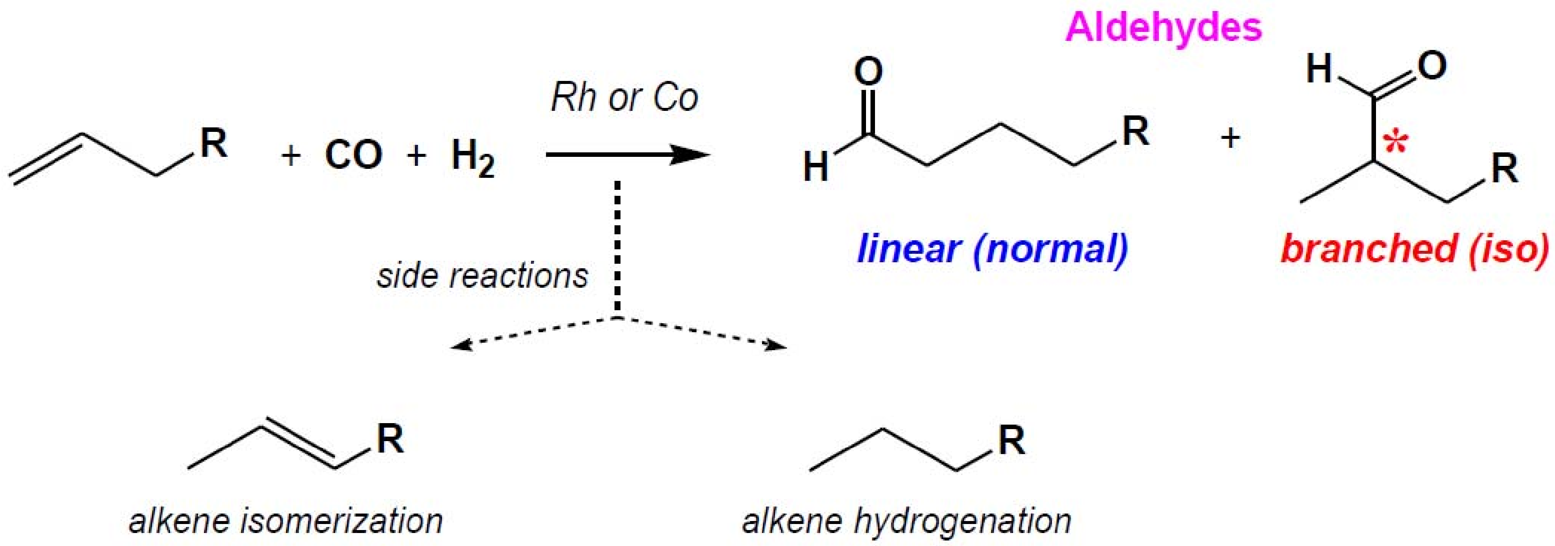


General scheme of the possibilities for HOMOGENEOUS CATALYSIS to **improve** in term of **usability and recyclability**

… the successful case of **hydroformilation**

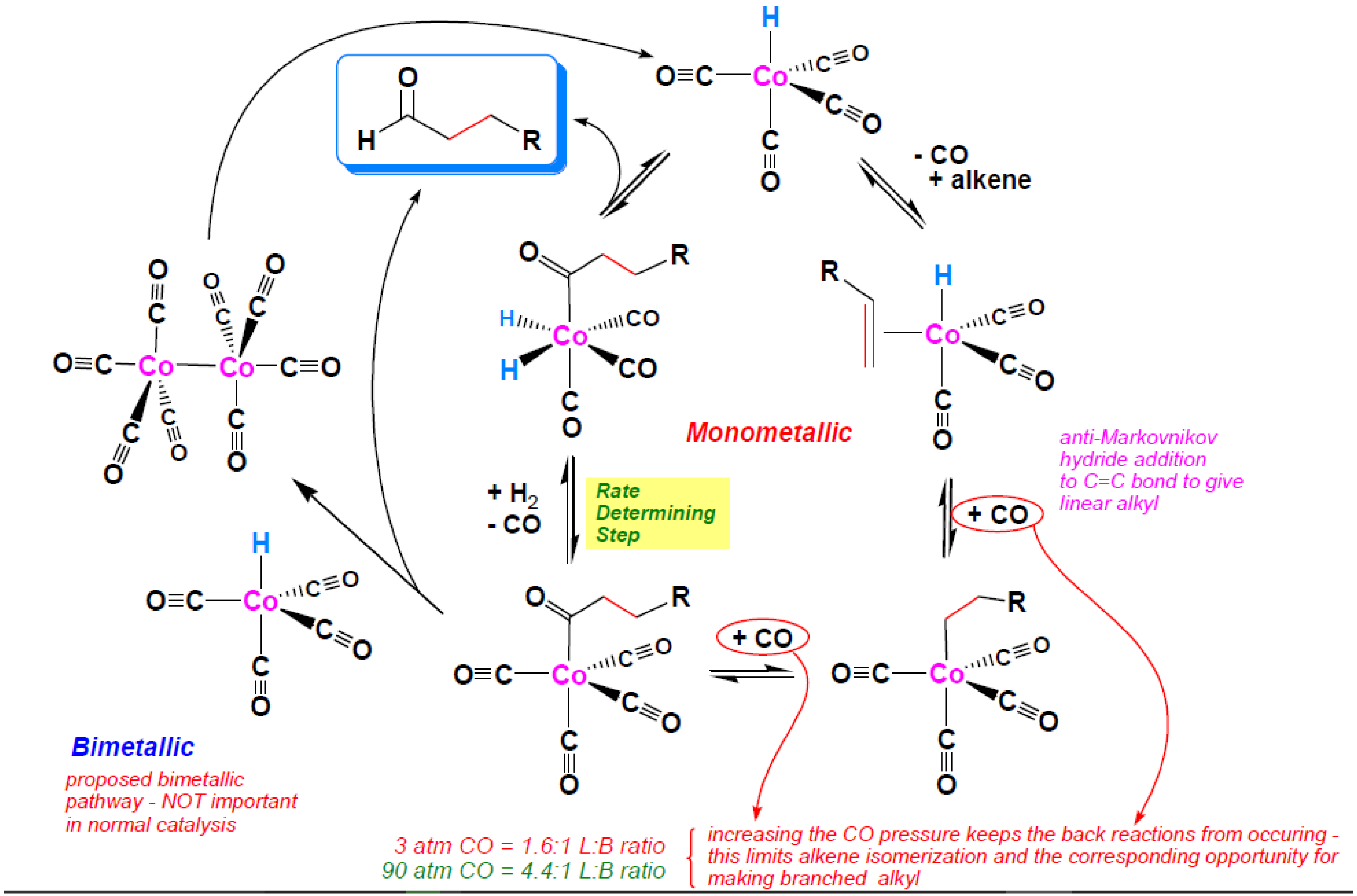
Hydroformilation from the beginning to multiphase approach

Hydroformylation (Oxo) Catalysis

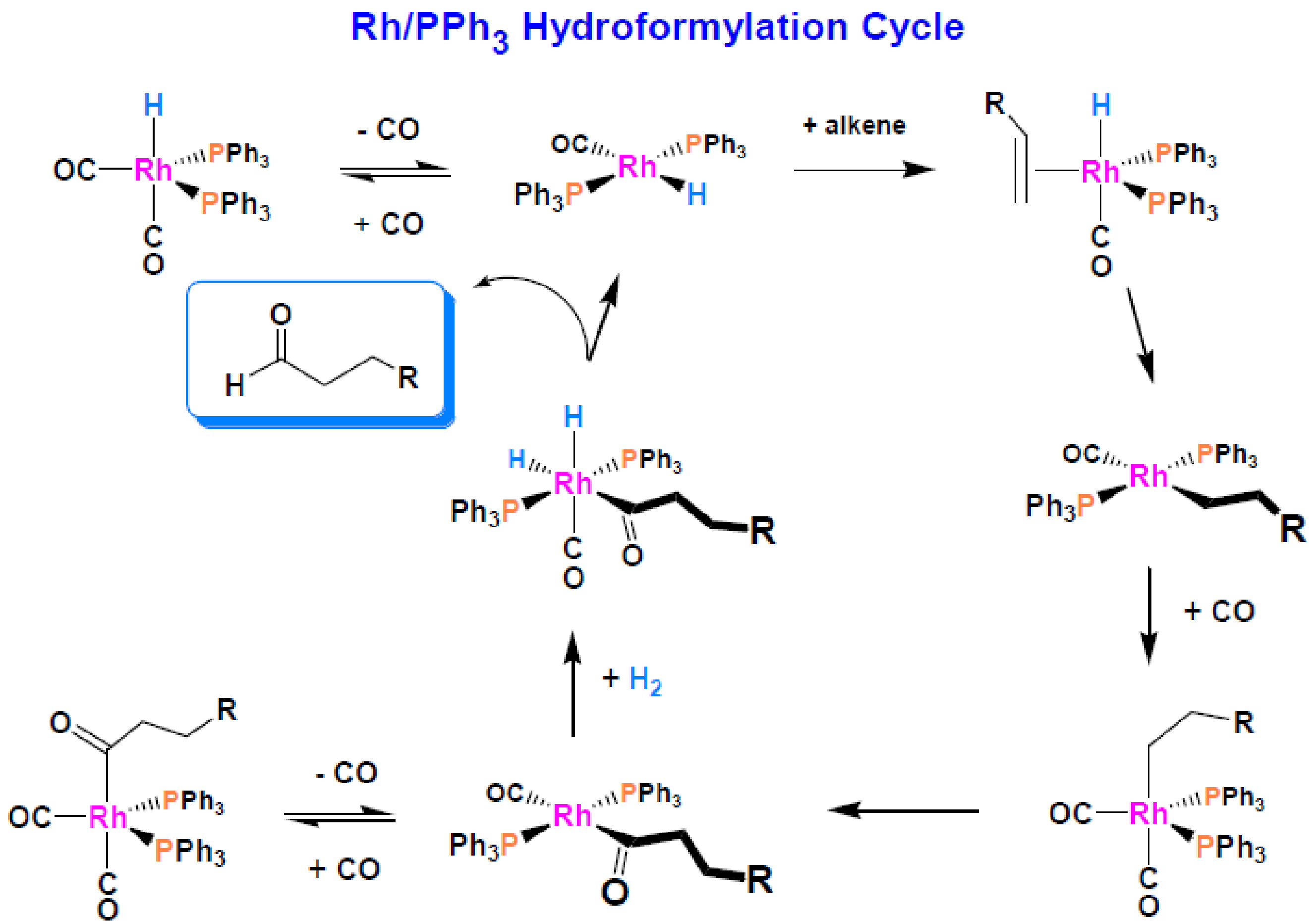


- **Largest homogeneous catalytic process**
- **> 15 billion pounds of aldehydes (alcohols) per year**
- **Commercial catalysts are complexes of Co or Rh**
- **Selectivity to linear (normal) or branched (iso) products is important**

A very complicated mechanism: «*a good run for homogeneous money*»

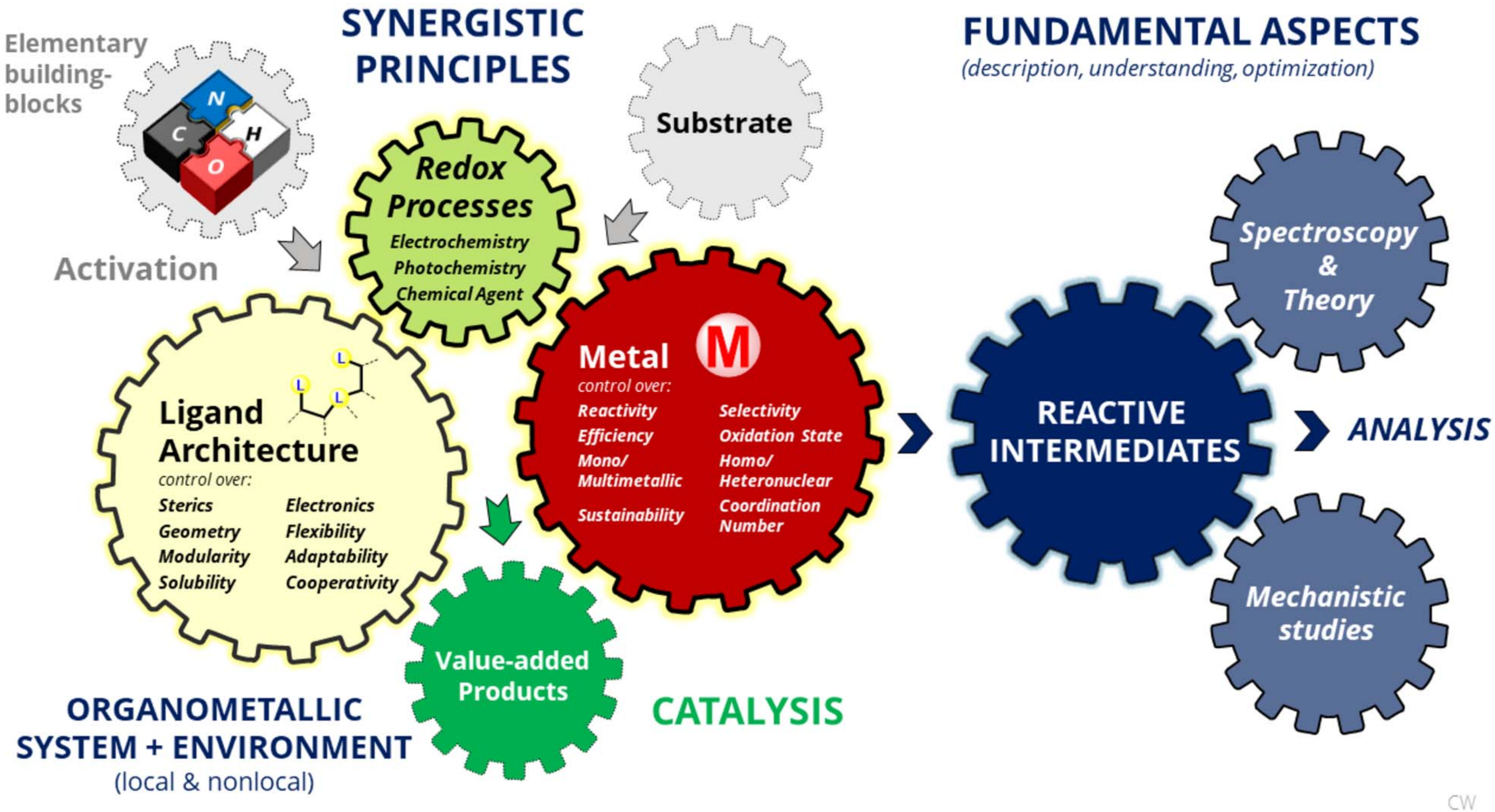


Hydroformilation: the rhodium generation

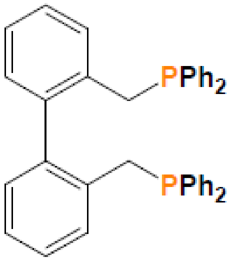


… … … efficiency (conditions and selectivity) refining toward COMMERCIALIZATION

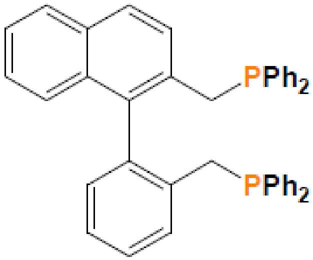
Relevance and tools for a molecular (homogeneous) catalyst design



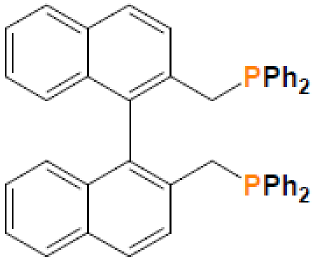
Rhodium based hydroformilation: the next generation



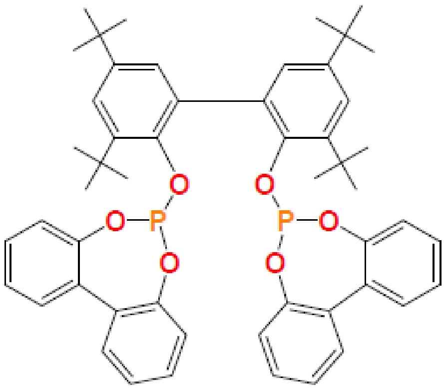
Bisbi



Bisbi*



Naphos



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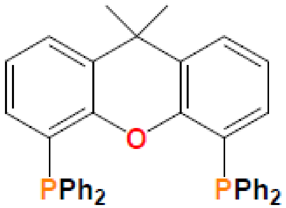


Xantphos

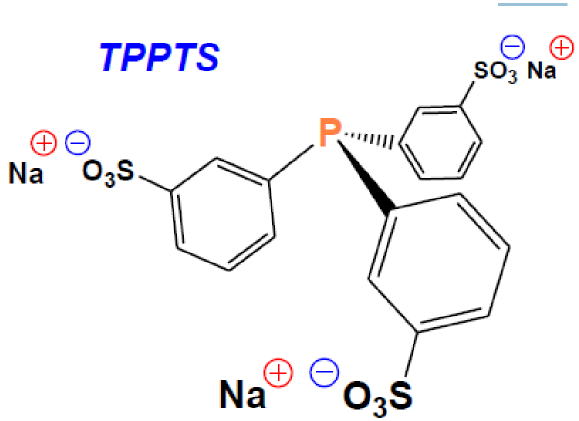
Catalyst (1 mM)	Init TOF (min^{-1})	Aldehyde L:B	% iso
Rh/PPh_3 (1:400)	13(1)	9:1	< 0.5
Rh/Bisbi (1:5)	25(2)	70:1	< 0.5
Rh/Naphos (1:5)	27(1)	120:1	1.5
Rh/Xantphos (1:5)	13(2)	80:1	5.0

A closely related bisphosphine ligand used by Herrmann and Beller (independently) for hydroformylation studies is Naphos (not to be confused with the Binap bisphosphine ligand that has the PPh_2 groups directly bonded to the naphthalene rings).

An excellent example of sustainable chemical homogeneous catalysis process
Ruhrchemie/Rhône-Poulenc’s (RCH/RPs) oxo process
a prototype of an aqueous biphasic process

Aqueous Biphase Operations

TPPTS



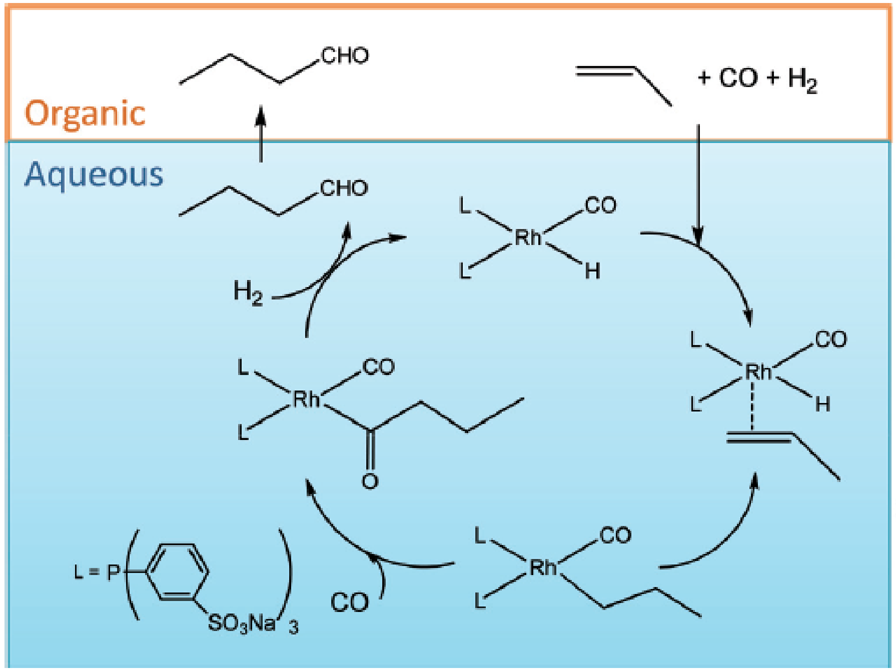
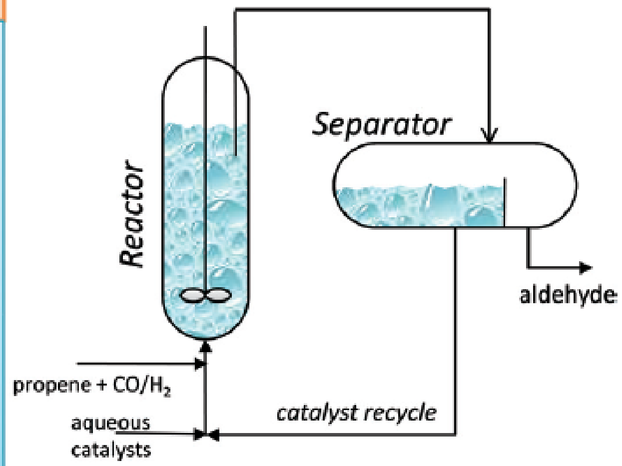
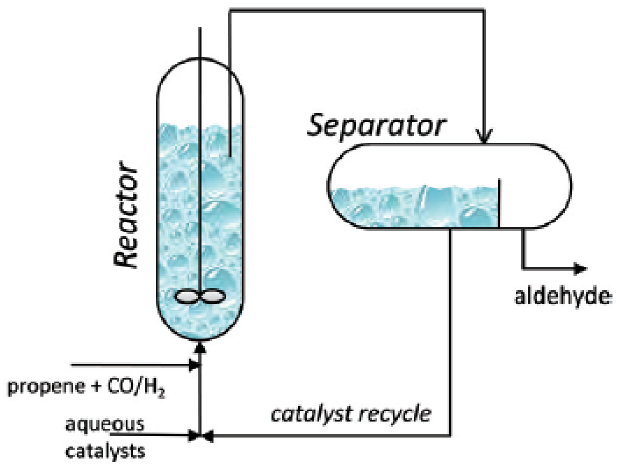


Figure 2.3 Ruhrchemie/Rhône-Poulenc hydroformylation process. Source: adapted from Sheldon *et al.* [2].



RCH/RP process vs. Co Catalysts

RCH/RP



- **Milder** reaction **conditions** (e.g. lower pressure);
- **reduction of energy consumption is obtained**;
- volume of **wastewater 70-times lower** than that for the Co-cat high pressure process

E-FACTOR < 0.1
total waste / product

Conventional oxo process: cobalt catalyst

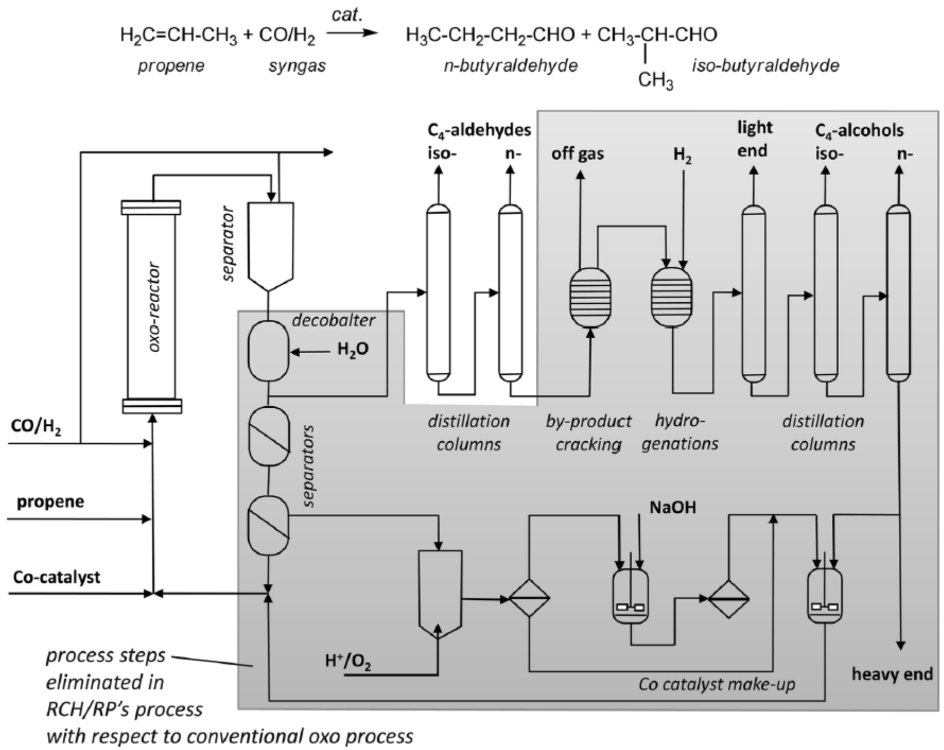
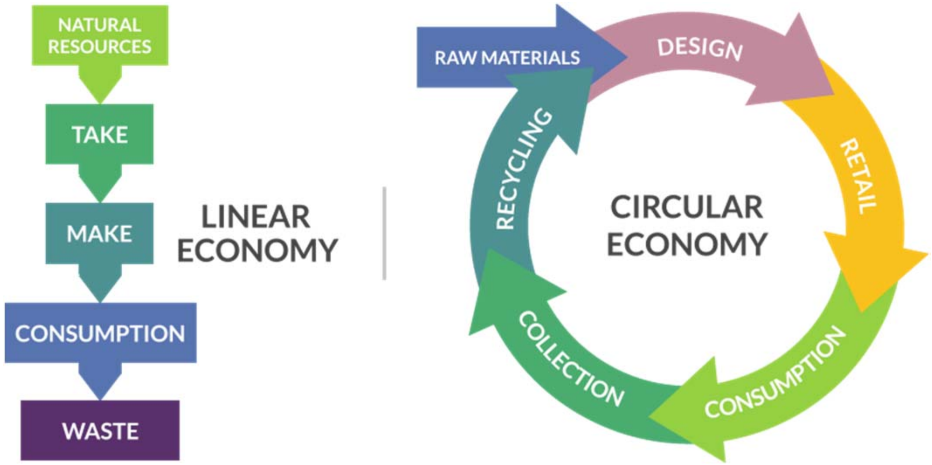


Figure 2.4 Schematic flow-sheet of a conventional oxo process, with an indication of the parts that are eliminated in the RCH/RPs process. Source: adapted from Cornils and Herrmann [65].

E-FACTOR 0.6-0.9
total waste / product

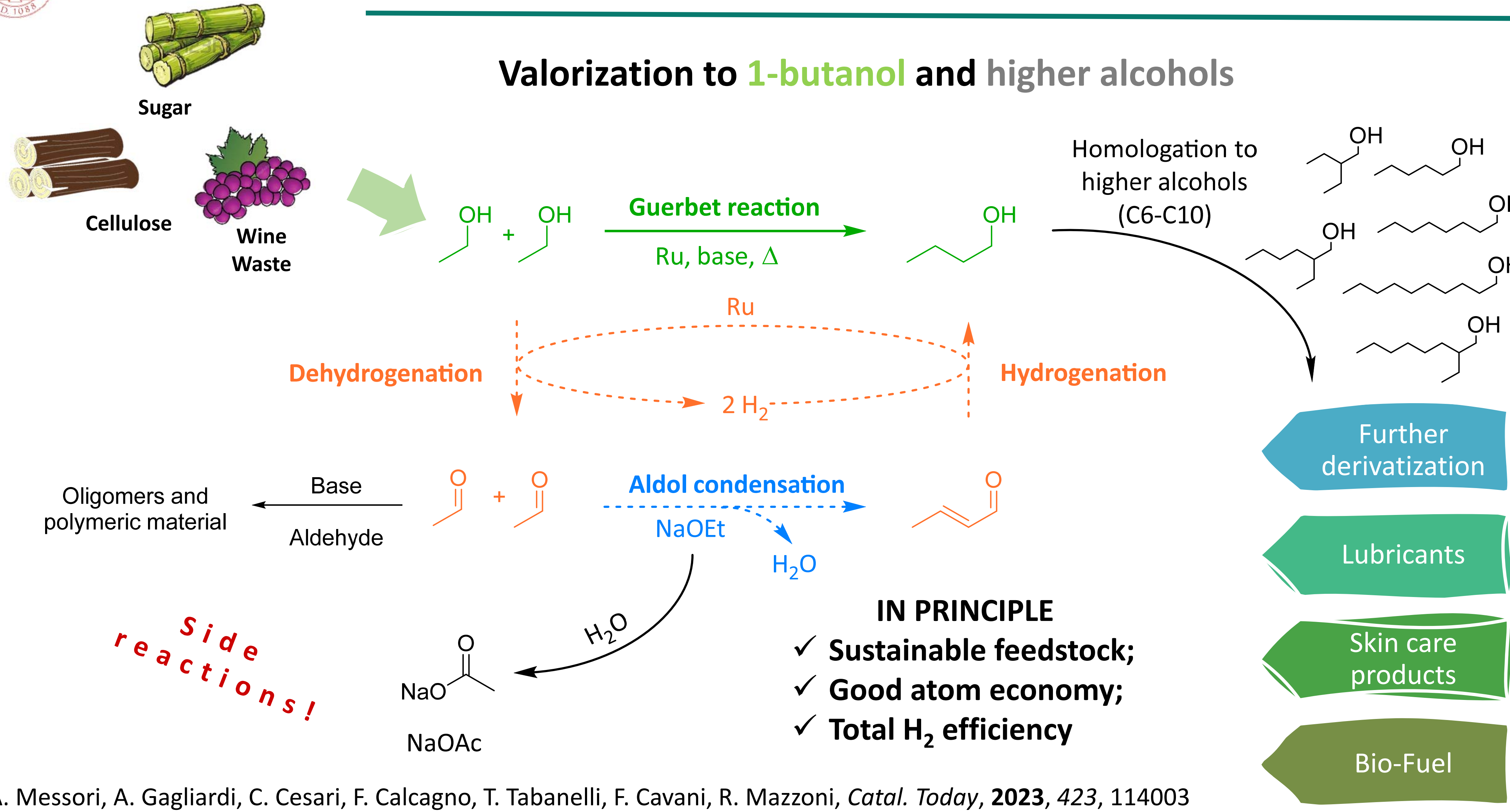
IS THERE ANY PLACE FOR THE DEVELOPMENT OF MORE SUSTAINABLE PROCESSES TO PRODUCE OXO-ALCOHOLS?

- **OXO-ALCOHOLS** SUCH AS BUTANOL ARE USUALLY PRODUCED **FROM FOSSIL FUELS** BY THE **OXO-PROCESS**;
- OTHERWISE THE **ABE PROCESS** EXPLOITS **ENZIMES CATALYSIS**;
- A CATALYTIC PROCESS THAT TRANSFORMS ETHANOL IN HIGHER ALCOHOLS IS KNOWN AS **GUERBET REACTION** THAT WOULD BE AN **IDEAL MECHANISM** FOR THE HOMOLOGATION OF ALCOHOL PURPOSES, BUT…
- THE REACTION STILL HAVE SOME **HEAVY DRAWBACKS**;
- LET'S RECALL A COUPLE OF SUSTAINABLE CONCEPTS: **WASTE REUSE AND CIRCULAR ECONOMY**



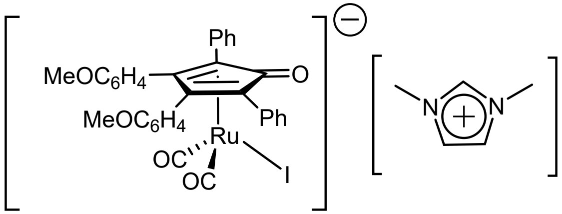
The Guerbet reaction: homogeneous catalysts, liquid phase

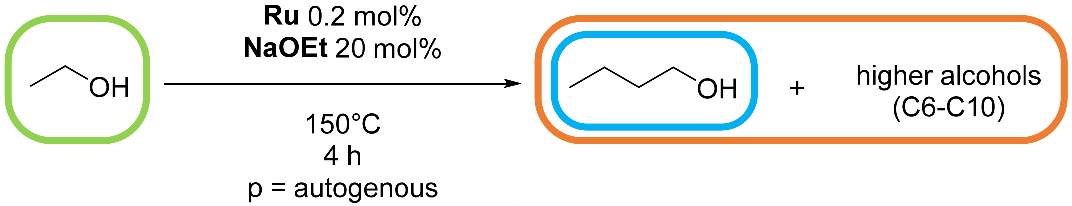
Valorization to 1-butanol and higher alcohols

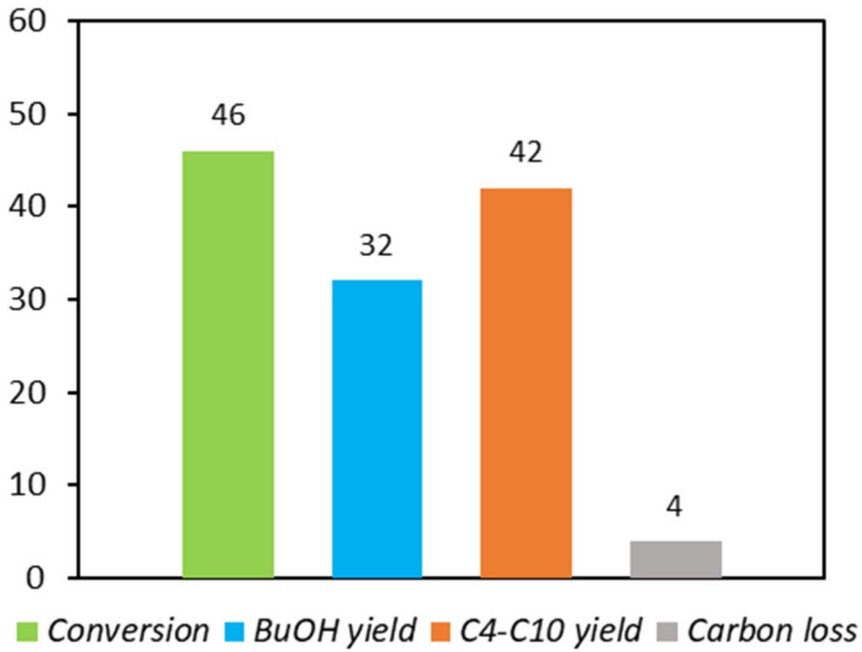


A. Messori, A. Gagliardi, C. Cesari, F. Calcagno, T. Tabanelli, F. Cavani, R. Mazzoni, *Catal. Today*, **2023**, *423*, 114003

OUR Ru-CATALYST







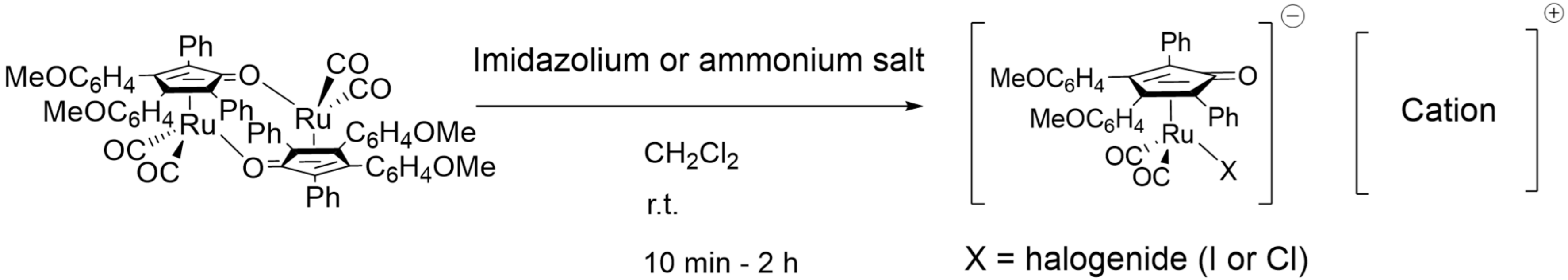
Solventless reaction performed by **Ru/NaOEt** system

The catalyst shows **water tolerance**

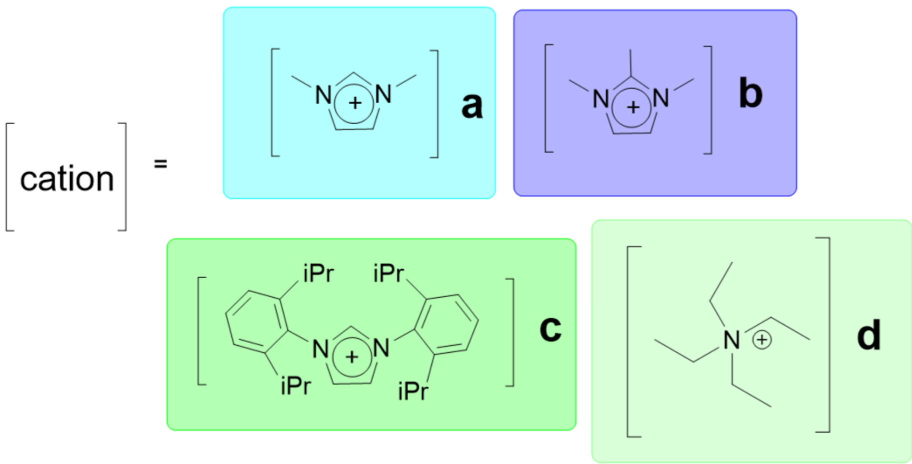
Ru catalyst can be **reused**

R. Mazzoni, C. Cesari, V. Zanotti, C. Lucarelli, T. Tabanelli, F. Puzzo, F. Passarini, E. Neri, G. Marani, R. Prati, F. Viganò, A. Conversano, F. Cavani, *ACS Sustainable Chem. Eng.* **2019**, *7*, 224.

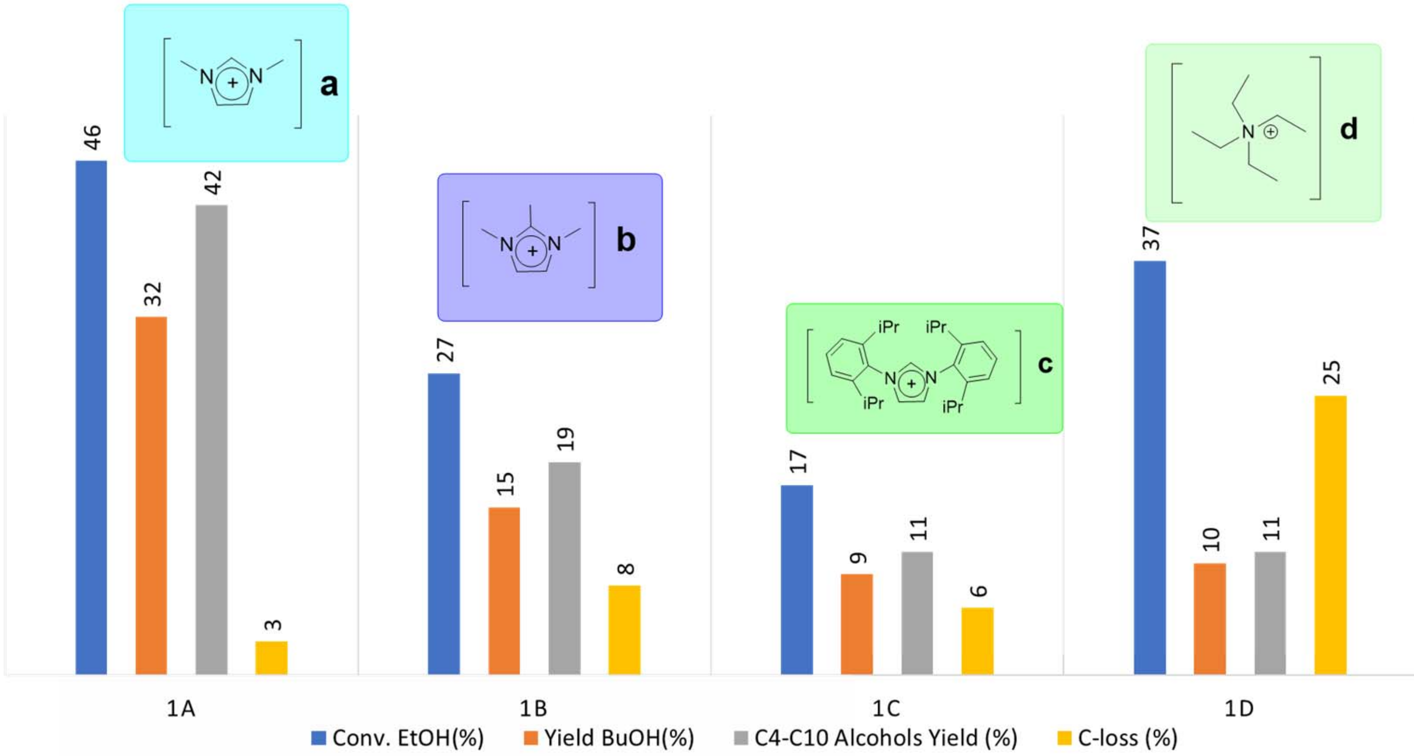
Ru-CATALYSTS: screening of the counterions



1a-d

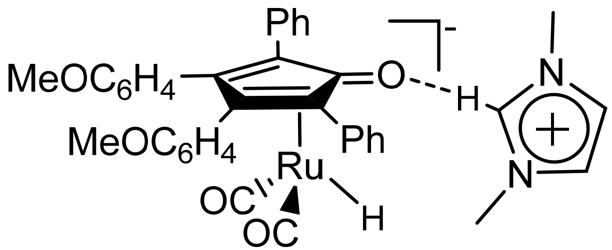


Ru-CATALYSTS: the role of steric encumbrance and of the hydrogen bond



DFT CALCULATION

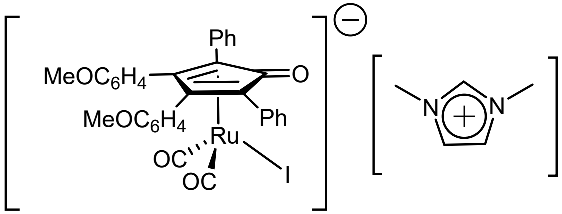
- **Hydrogen bond** improve the stability of the tight ion pair and of the active species;
- Steric hinderance disfavour the hydrogen bond.

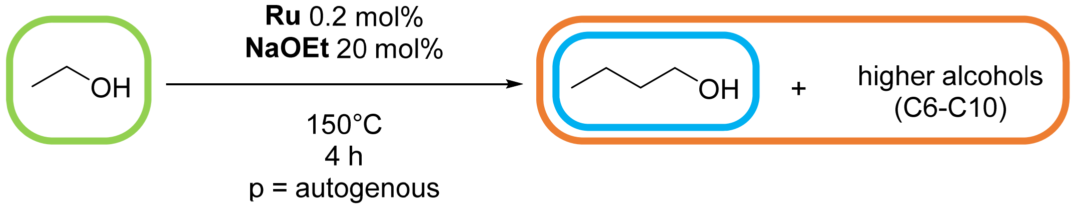


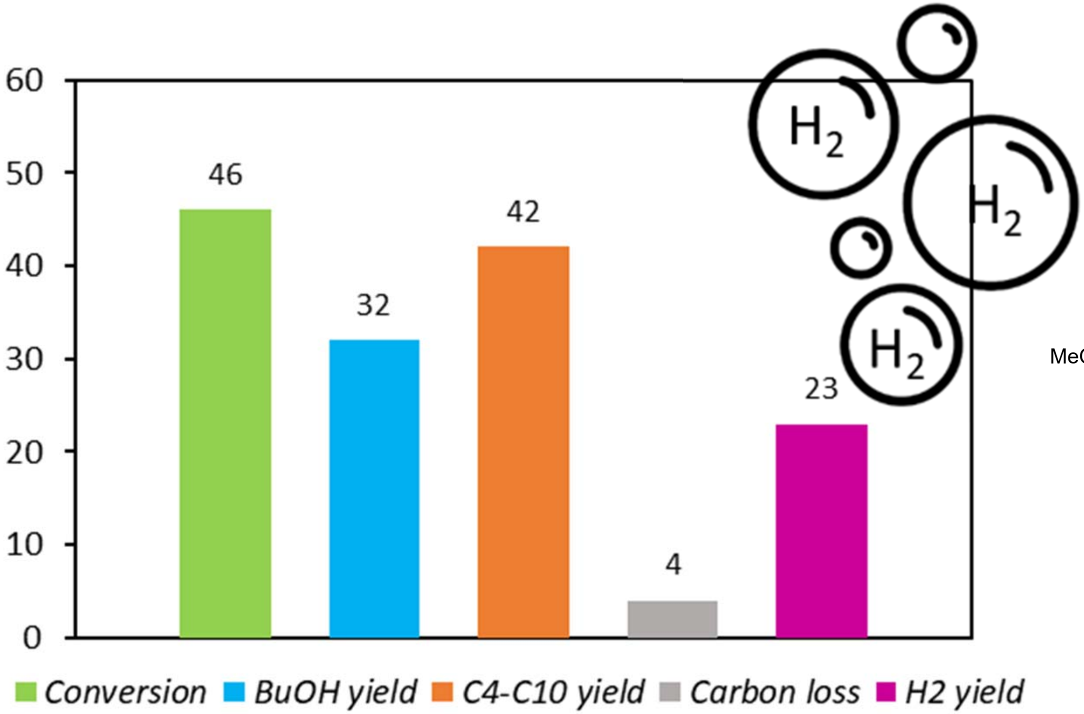
Ru-H

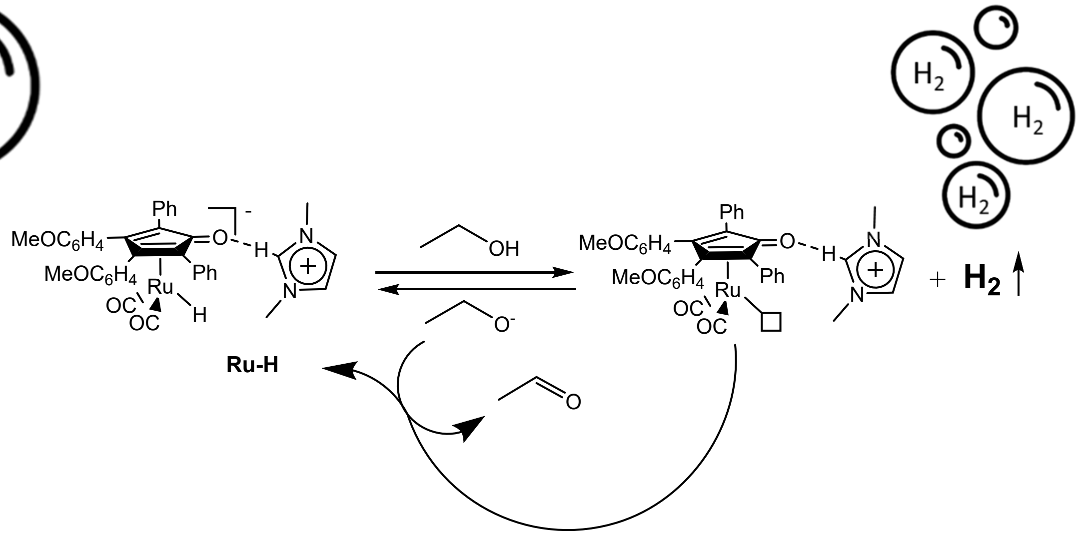
✓ The best catalyst active species

H_2 PRODUCTION: UNEXPECTED «SIDE» REACTION

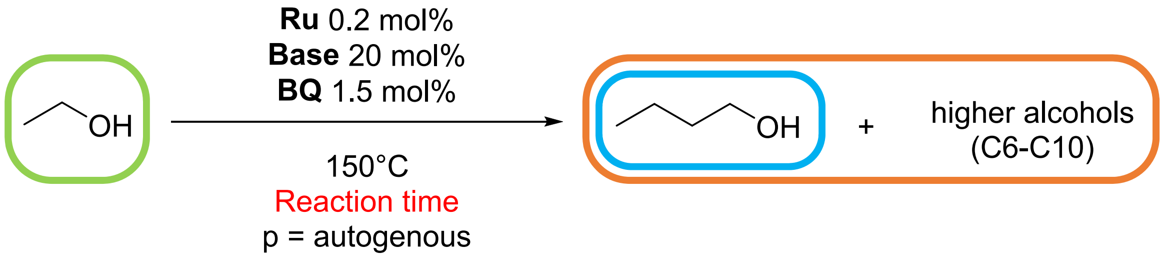




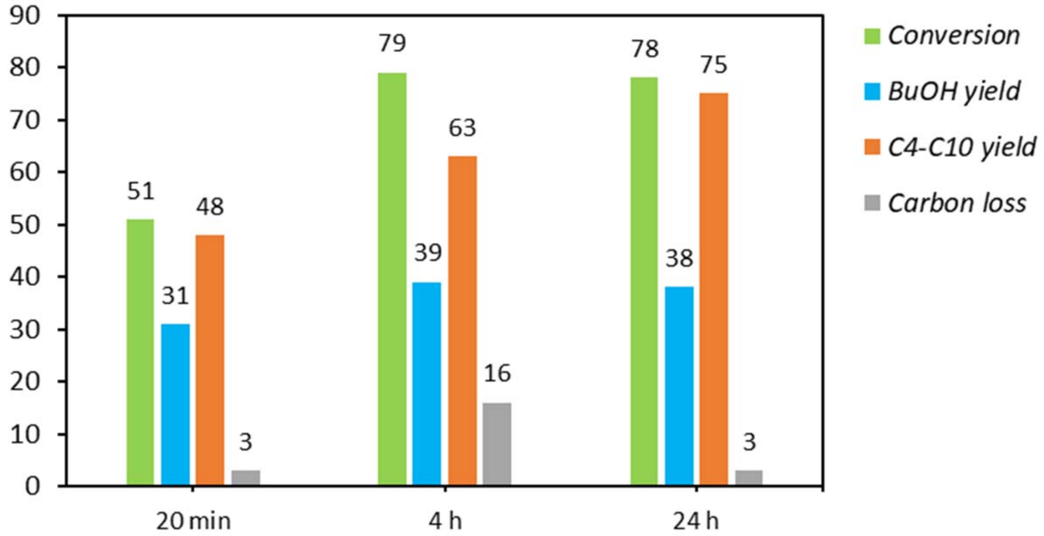


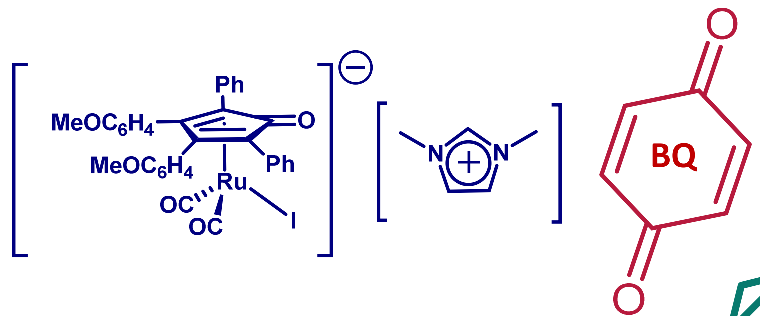


BENZOQUINONE: A BIO-MIMETIC COOPERATIVE CO-CATALYST



Reaction Time





Guerbet by Ru/BQ/NaOEt system:

- ✓ **Solventless;**
- ✓ **Water tolerant;**
- ✓ **Recyclable;**
- ✓ **Faster (4-120 times vs SoA);**
- ✓ **More efficient (30% increased conversion vs Ru/NaOEt);**
- ✓ **Highly selective;**
- ✓ **Suppress side H_2 production**

Cesari, C.; Gagliardi, A.; Messori, A.; Monti, N.; Zanotti, V.; Zacchini, S.; Rivalta, I.; Calcagno, F.; Lucarelli, C.; Tabanelli, T.; Cavani, F.; Mazzoni, R. *J. Catal.* **2022**, *405*, 47

Patent WO2019193079 (A1)

MOVING TO THE LARGER AND THE GREENER

TUNING THE SELECTIVITY BY CHANGING THE HEADSPACE

Headspace volume decrease

V liq (ml)	Vr (ml)	V_{liq}/V_r (%)	Conv. EtOH (%)	BuOH yield (sel.) %	C_6-C_{10} yield (sel.) %	H_2 yield (%)	C-loss (%)
0.5	53.8	0.9	76.0	27.4 (36)	26.1 (34)	24.4	22.5
0.5	13.4	3.7	77.3	33.8 (44)	30.6 (40)	16.7	12.9
0.5	7.5	6.7	71.3	38.6 (54)	27.2 (38)	9.2	5.6
1	7.5	13.3	63.2	41.0 (65)	20.3 (32)	9.7	1.9

- ✓ **Butanol selectivity increase**
- ✓ **H_2 yield decrease**
- ✓ **Better carbon balance**

- ✓ Best configuration: use of **waste biomasses** and in an integrated cogeneration unit.
- ✓ Enabling the recovery of the catalytic system **up to five cycles** to scenario: **reduction** in the impacts **higher than 50%** for the categories of **global warming potential**, **- 41%** for the **mineral resource scarcity** and around **-16%** for the **fine particulate matter** formation.

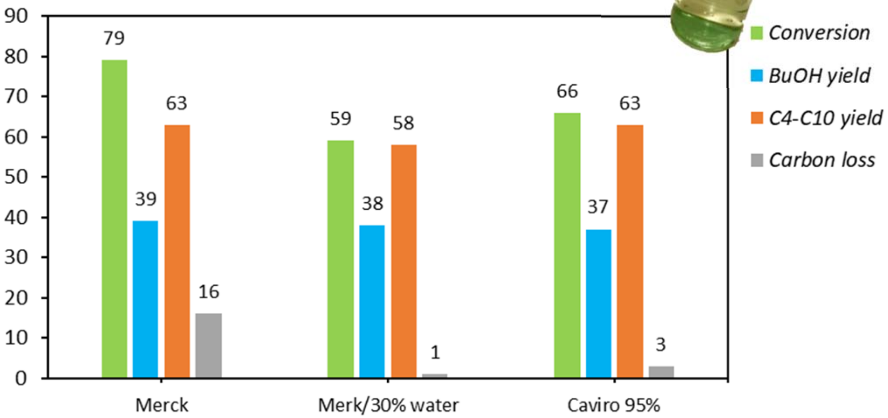
A. Piazzi, T. Tabanelli, A. Gagliardi, F. Cavani, C. Cesari, D. Cespi, F. Passarini, A. Conversano, F. Viganò, D. Di Bona, R. Mazzoni, *Sust. Chem. Pharm.*, **2023**, 35, 101222

TRASFERABLE TO A REAL MATRIX and RECYCLABLE

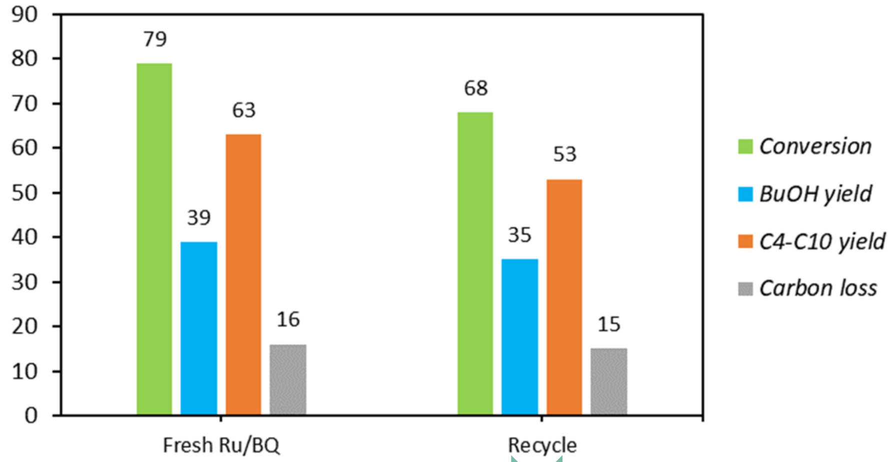
✓ **THE CATALYTIC PROCESS CAN BE TRANSFERRED TO A MATRIX OF WINE WASTES FURNISHED BY CAVIRO S.P.A.**

Heads and tails from ethanol distillation

Impurities	Amount (mg/100 mL)
Acetaldehyde	73.20
Methanol	127.93
Acetal	512.85
1-Propanol	383.52
Isobutanol	77.35
2-Butanol	4.55
Isoamyl alcohol	0.19
Ethyl acetate	98.85
Isoamyl acetate	0.25
2-Butanone	2.41
Allyl alcohol	0.18



✓ **CATALYST SYSTEM RECYCLE**

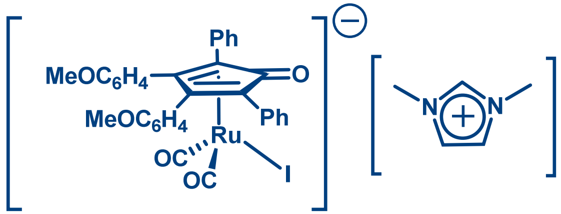


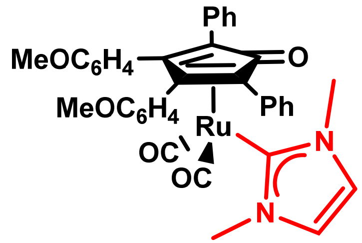
1) Catalytic run
2) **Remove** alcohol mixture
3) **Re-load** fresh EtOH/NaOEt
4) Catalytic run

Problems still to be solved:
- ❑ high amount of base;
- ❑ multiple recycling

MECHANISTIC INSIGHT

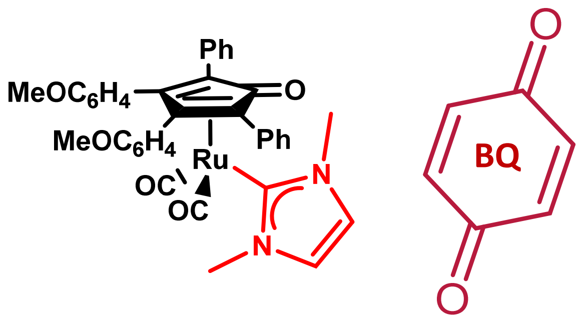
FROM IONIC TO COVALENT CATALYST



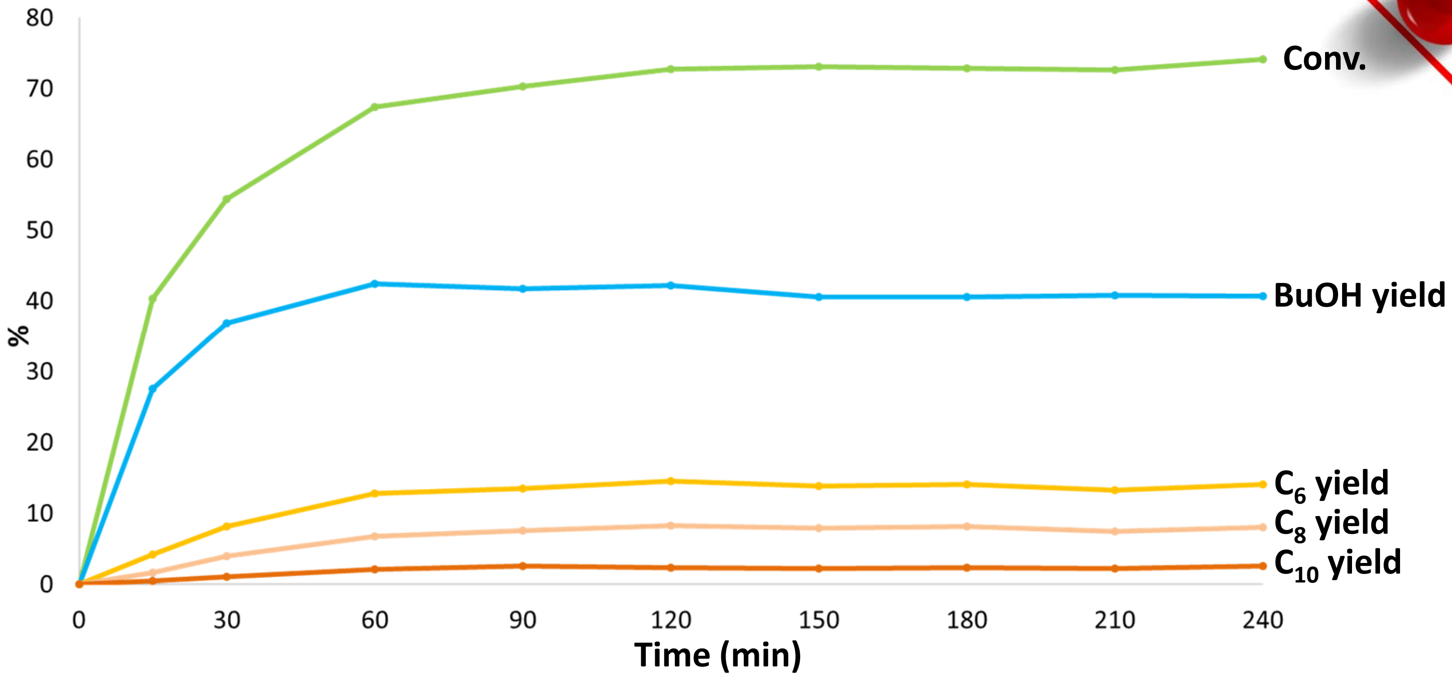


- ✓ The NHC catalyst is more efficient (down to 0.02% loading);
- ✓ The catalyst can be recycled;
- ✓ Neutral complex, easier DFT calculation

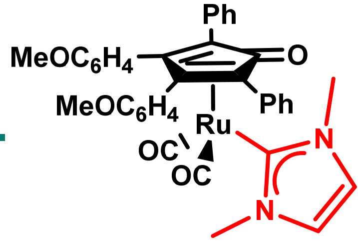
✓ The co-catalyst BQ still boosts conversion and yield.



T = 150°C; Cat = 0,2% ;
NaOEt = 20% ; BQ = 0,5%



MECHANISTIC INSIGHT: Ru CATALYST ACTIVATION



ACTIVATION *via* CO DISSOCIATION

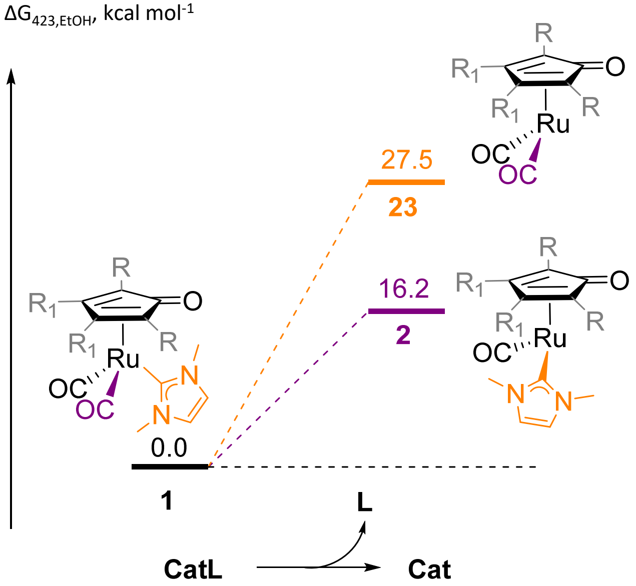
PREDICTED BY COMPUTATIONS

COMPUTATIONS: DFT methodology

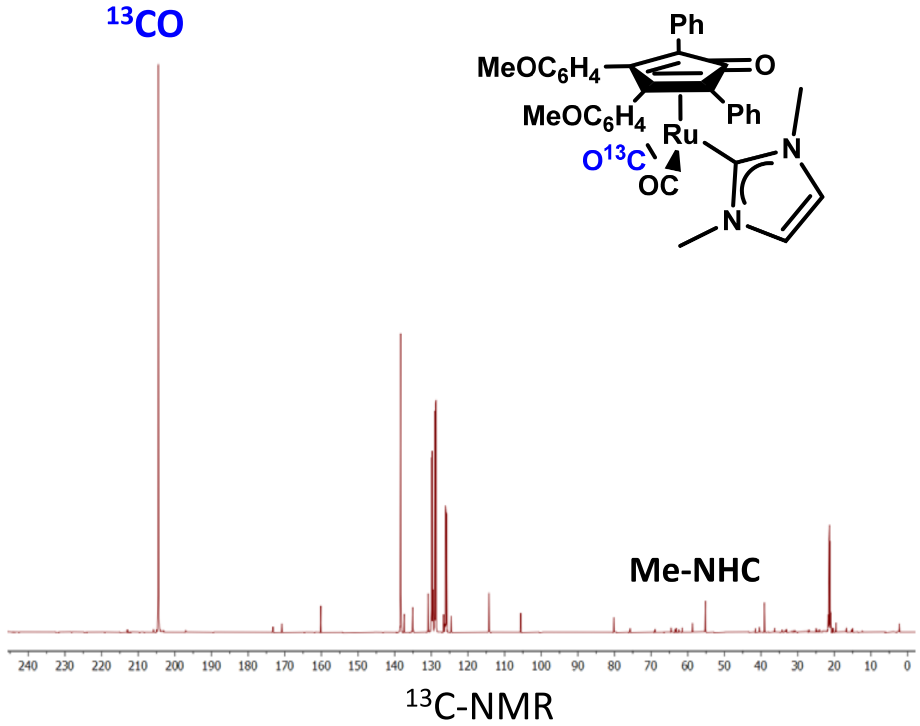
B3LYP/LANL2DZ/6-31G(d,p)//

B3LYP/LANL2DZ/6-311+G(2d,2p),

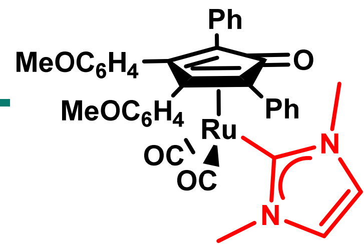
$\Delta G_{423,EtOH}$, kcal mol^{-1}



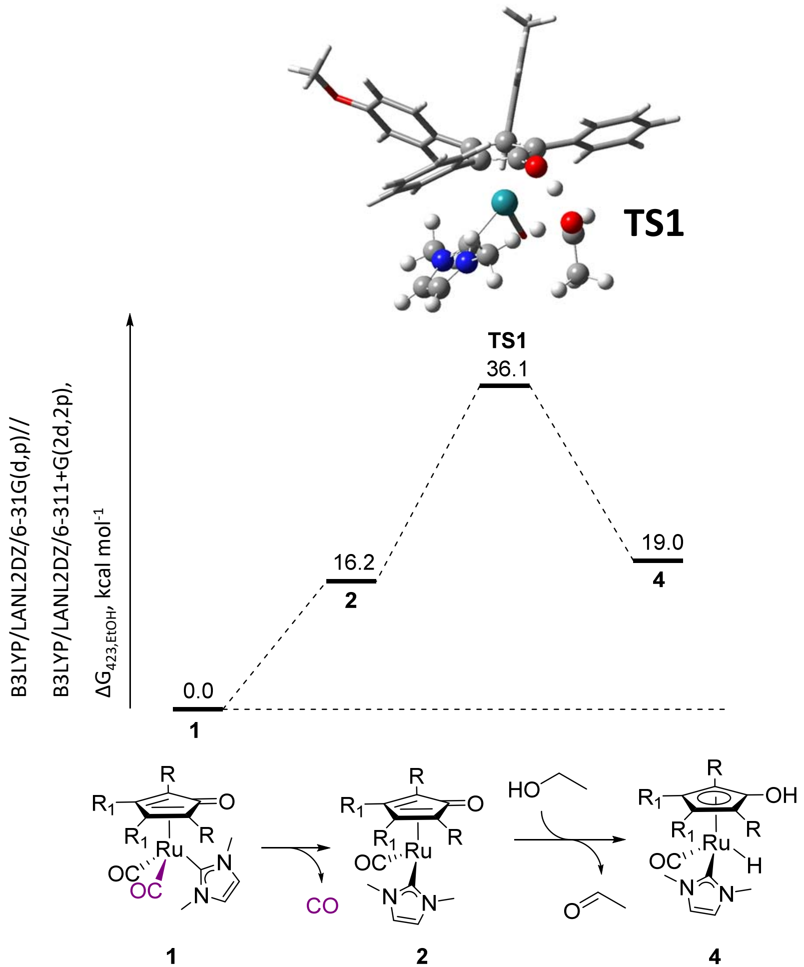
CONFIRMED BY ^{13}CO LABELLED NMR EXPERIMENTS



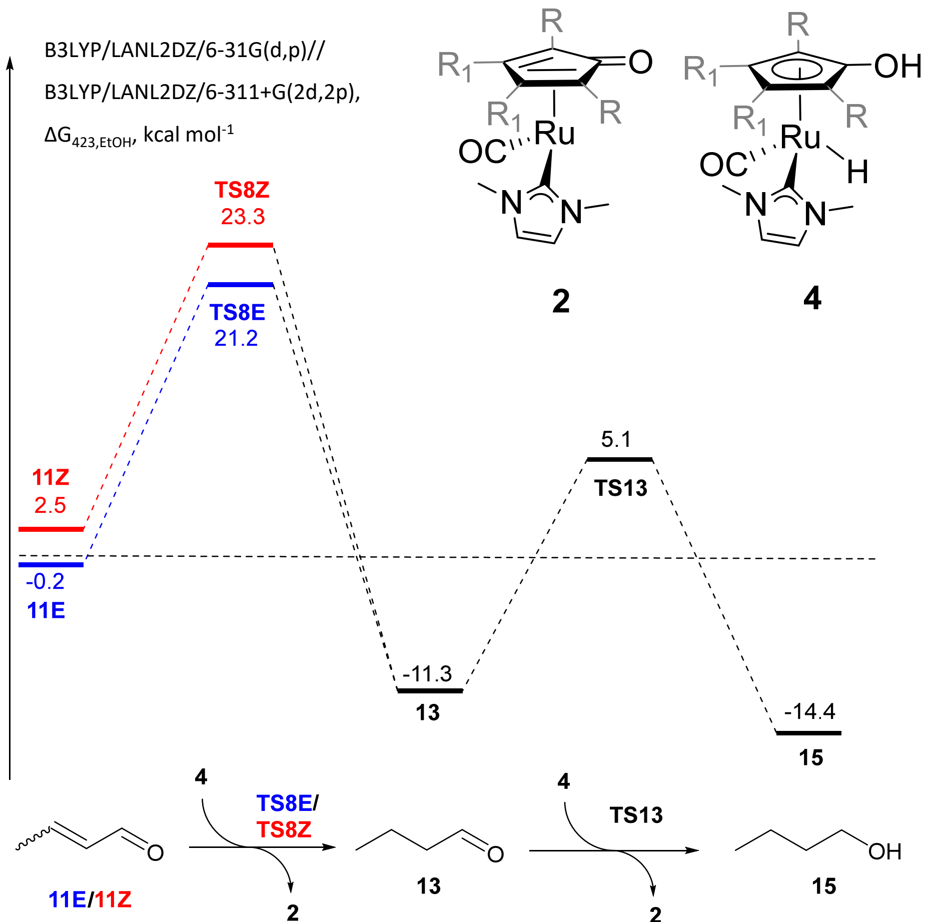
MECHANISTIC INSIGHTS: (DE)HYDROGENATION BY Ru-CAT



DEHYDROGENATION



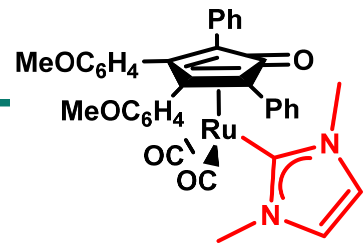
DOUBLE HYDROGENATION



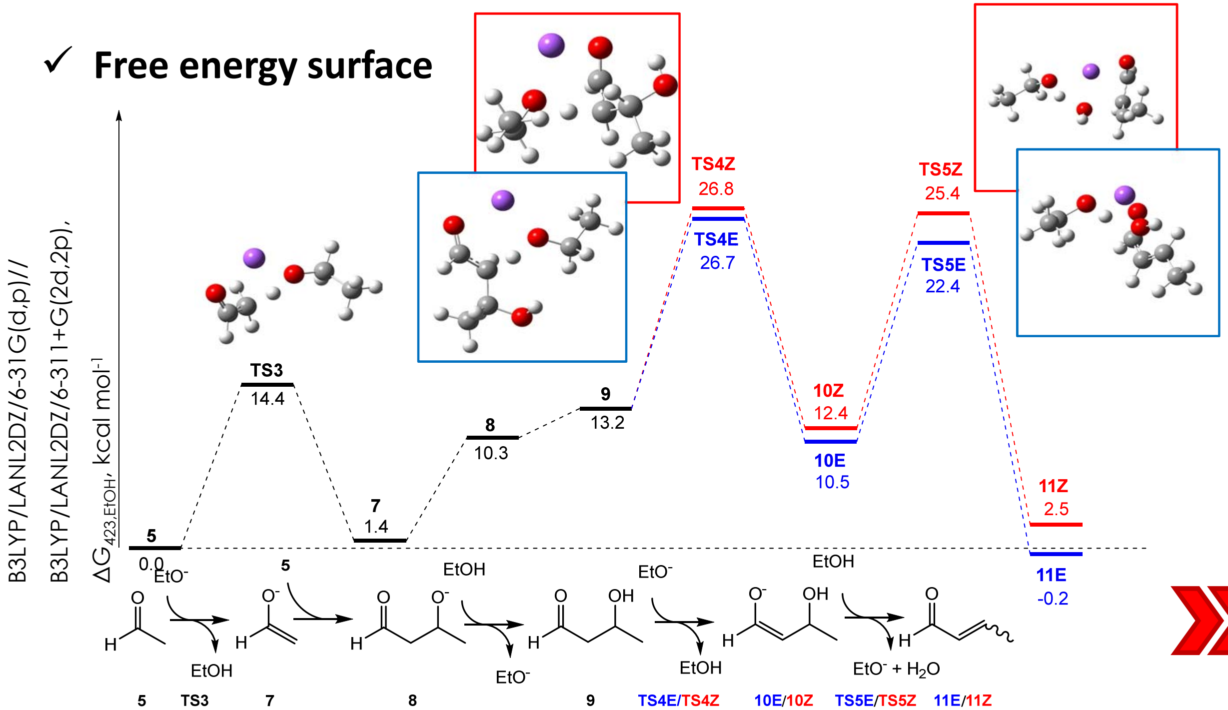
13 seems to be the most favored intermediate, also by GC-MS analysis.

To get **15** from **11E**/**11Z** there are 16 possible pathways.

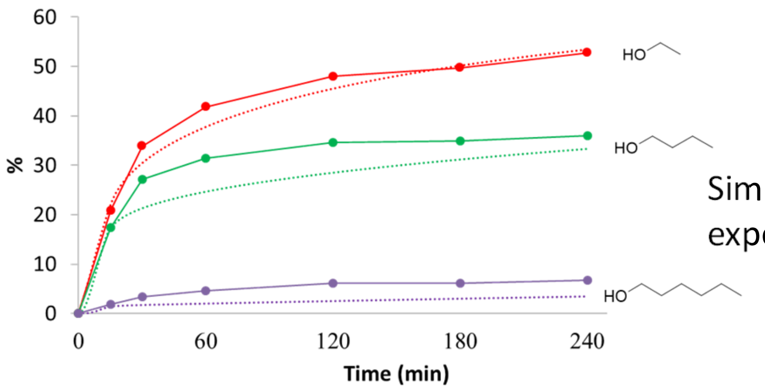
MECHANISTIC INSIGHTS: THE COMPLETE CYCLE



✓ Free energy surface

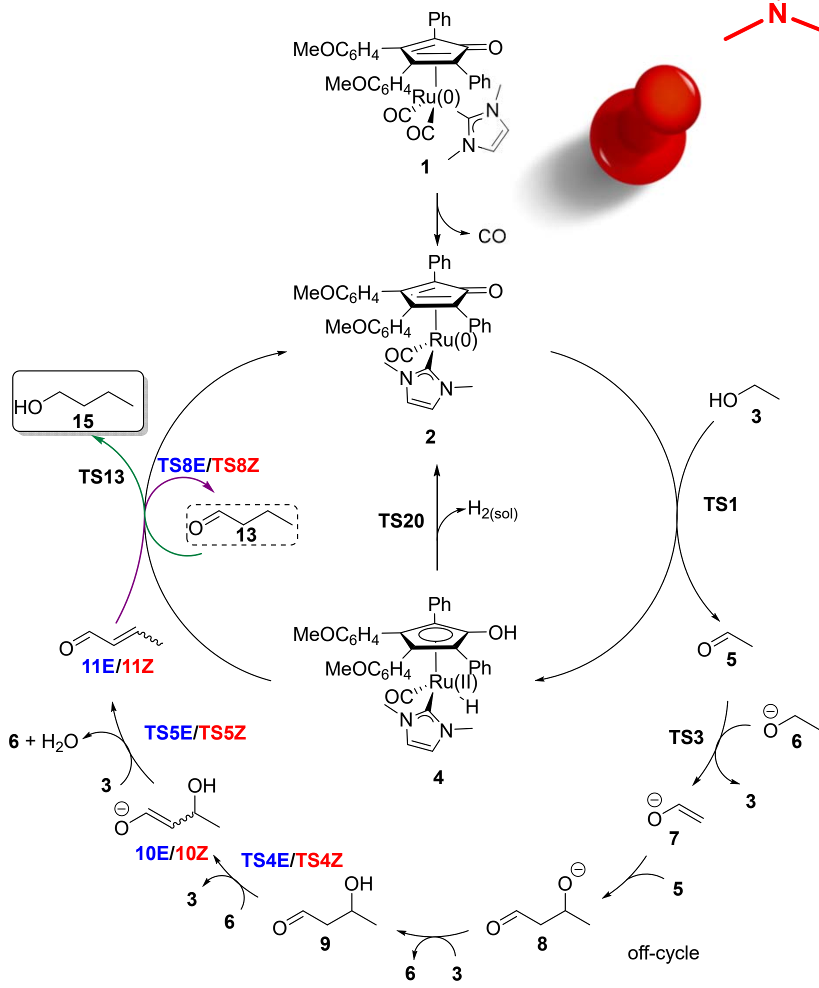


✓ Supported by kinetic model



Simulated (**dashed lines**)
experimental (**solid lines**)

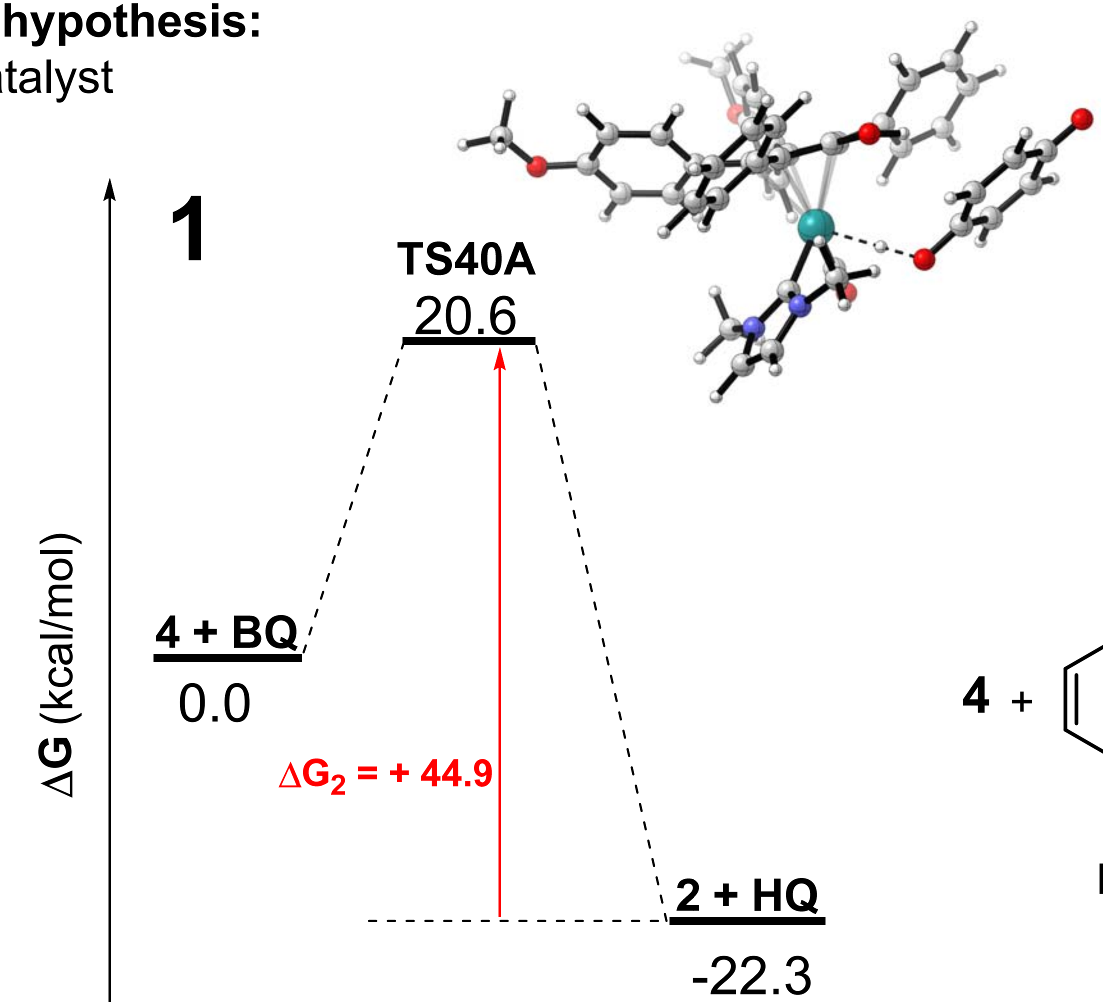
✓ The mechanism

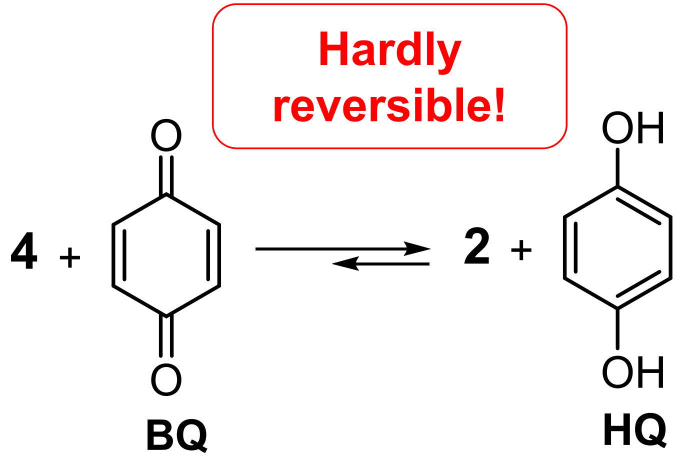


Manuscript in preparation

THE ROLE OF BENZOQUINONE: TWO HYPOTHESES

1) Hydrogen storage hypothesis:
BQ is reduced by the catalyst to hydroquinone (HQ).

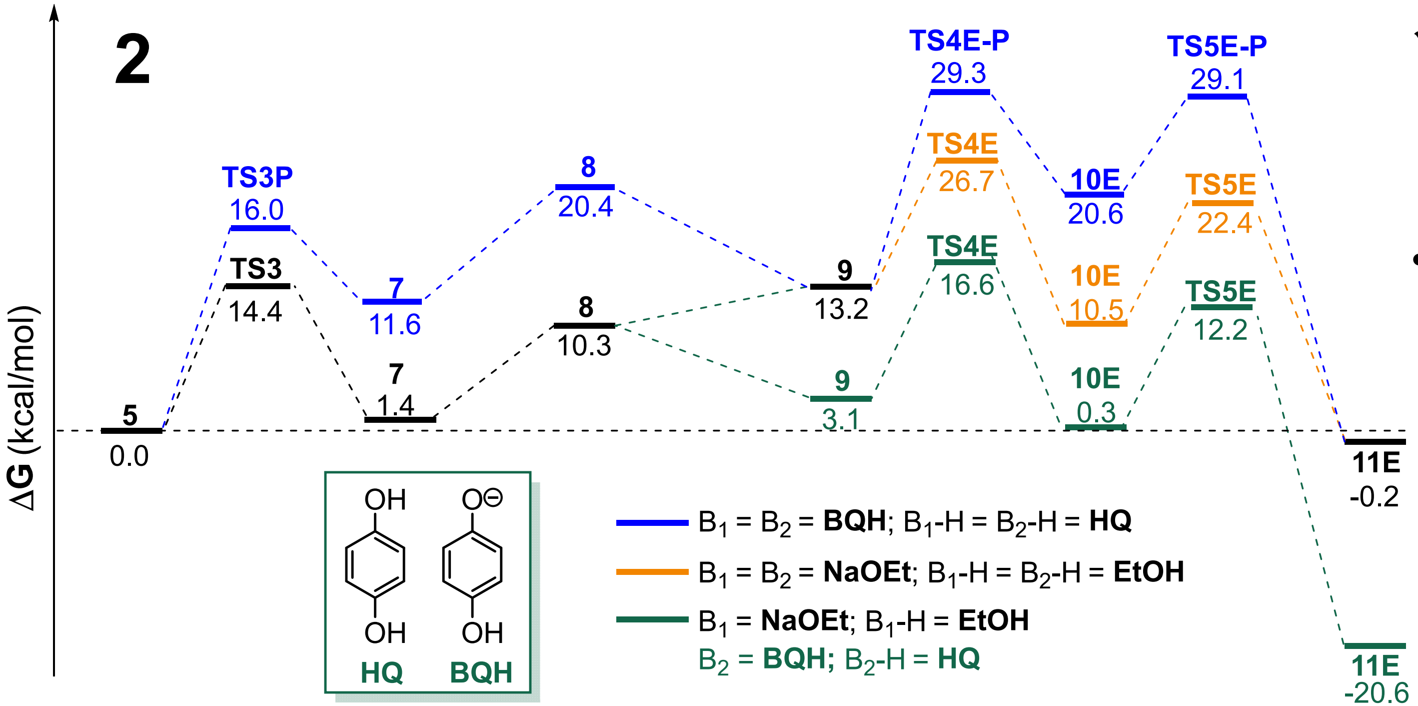


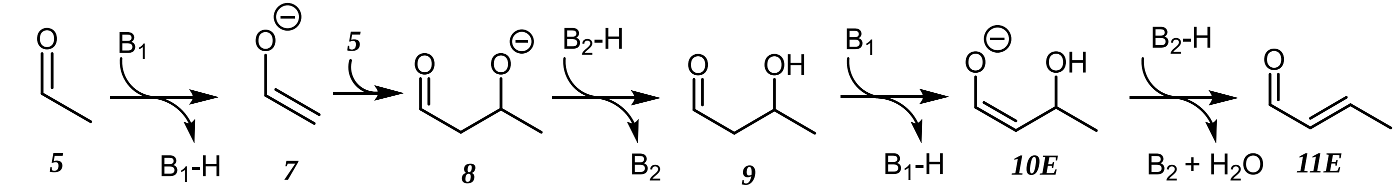


B3LYP/6-31G(d,p)//
B3LYP/6-311g++(2d,2p),
$\Delta G_{150°C, PCM}$

THE ROLE OF BENZOQUINONE: TWO HYPOTHESES

2) Mixed mechanism for aldol condensation: hydroquinone replaces ethanol as proton source in the C-C coupling mechanism.





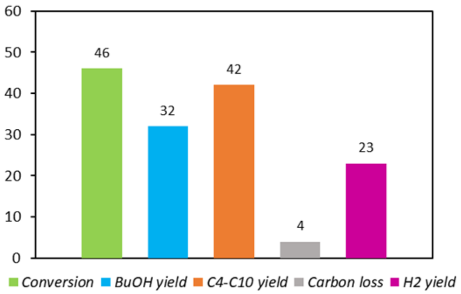
THEORETICAL OUTCOME

- ✓ **Aldol condensation catalysed by NaOEt + BQ/HQ shows a by far lower energy than the sole NaOEt;**
- **Sole BQH is even more unfavored**

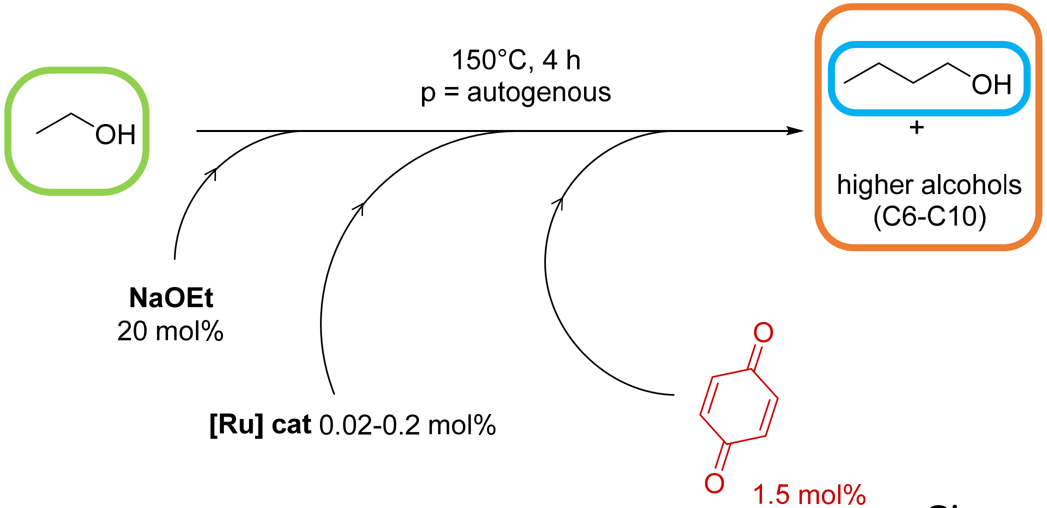
THEORETICAL SUGGESTIONS

- ❑ **BQ/HQ is likely to compete with the Cannizzaro side reaction.**
- ❑ **Acidity of the co-catalyst is likely to improve the efficiency**

Concluding remarks



Solventless reaction performed by **Ru/NaOEt** system



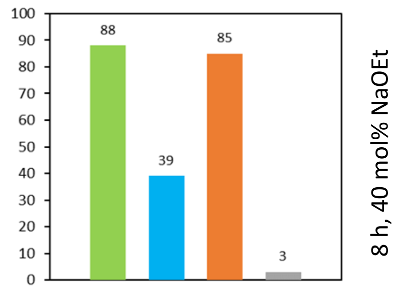
The reaction shows water tolerance

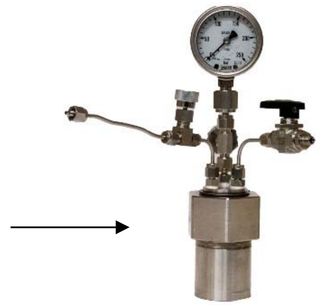
Ru can be reused

The catalytic process can be transferred to a matrix of wine wastes

"Mixed mechanism" system favor aldol condensation and reduce hydrogen evolution

Gives an impressive boost to the reaction





Selectivity tuning

Future perspective

- Immobilization towards heterogeneous catalysis

to

- Improve recycle
- Design by calculation

to

- Further Improve the catalysts productivity

Acknowledgments

CENTER FOR CHEMICAL CATALYSIS

CIRI FONTI RINNOVABILI, AMBIENTE, MARE ED ENERGIA - FRAME

Prof. Valerio Zanotti
Prof. Fabrizio Cavani
Dr. Cristiana Cesari
Dr. Tommaso Tabanelli
Dr. Carlo Lucarelli
Dr. Anna Gagliardi
Dr. Alessandro Messori
Dr. Andrea Piazzi
Dr. Massimiliano Curcio
Dr. Nicola Monti
Dr. Giacomo Corelli

DFT
Prof. Ivan Rivalta
Dr. Francesco Calcagno

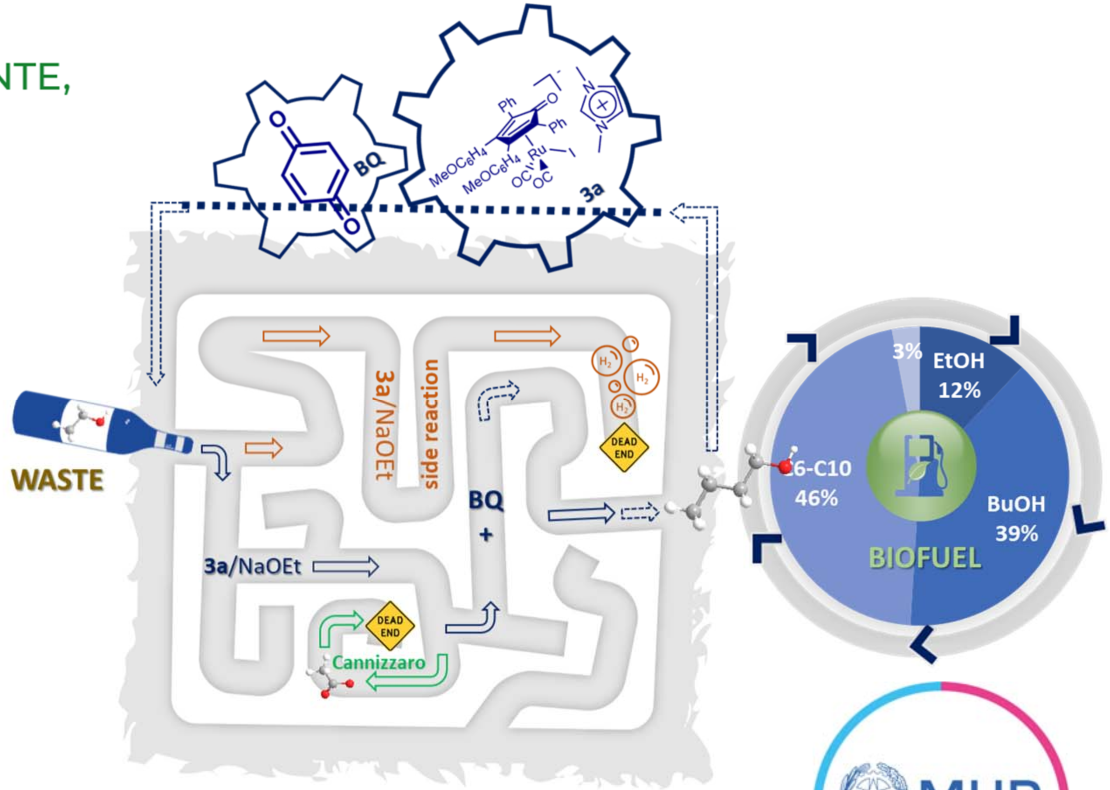
LCA
Prof. Fabrizio Passarini
Dr. Daniele Cespi

CAVIRO DISTILLERIE

Ing. Giovanni Marani
Dott.ssa Rosa Prati

LEAP Laboratorio Energia e Ambiente Piacenza

Prof. Federico Viganò
Antonio Conversano



VALSOVIT
Valorizzazione sostenibile degli scarti della filiera vitivinicola per l'industria chimica e salutistica

POC-Unibo
POC-MISE

MUR Ministero dell'Università e della Ricerca
PRIN 2022 - ALCOVAL

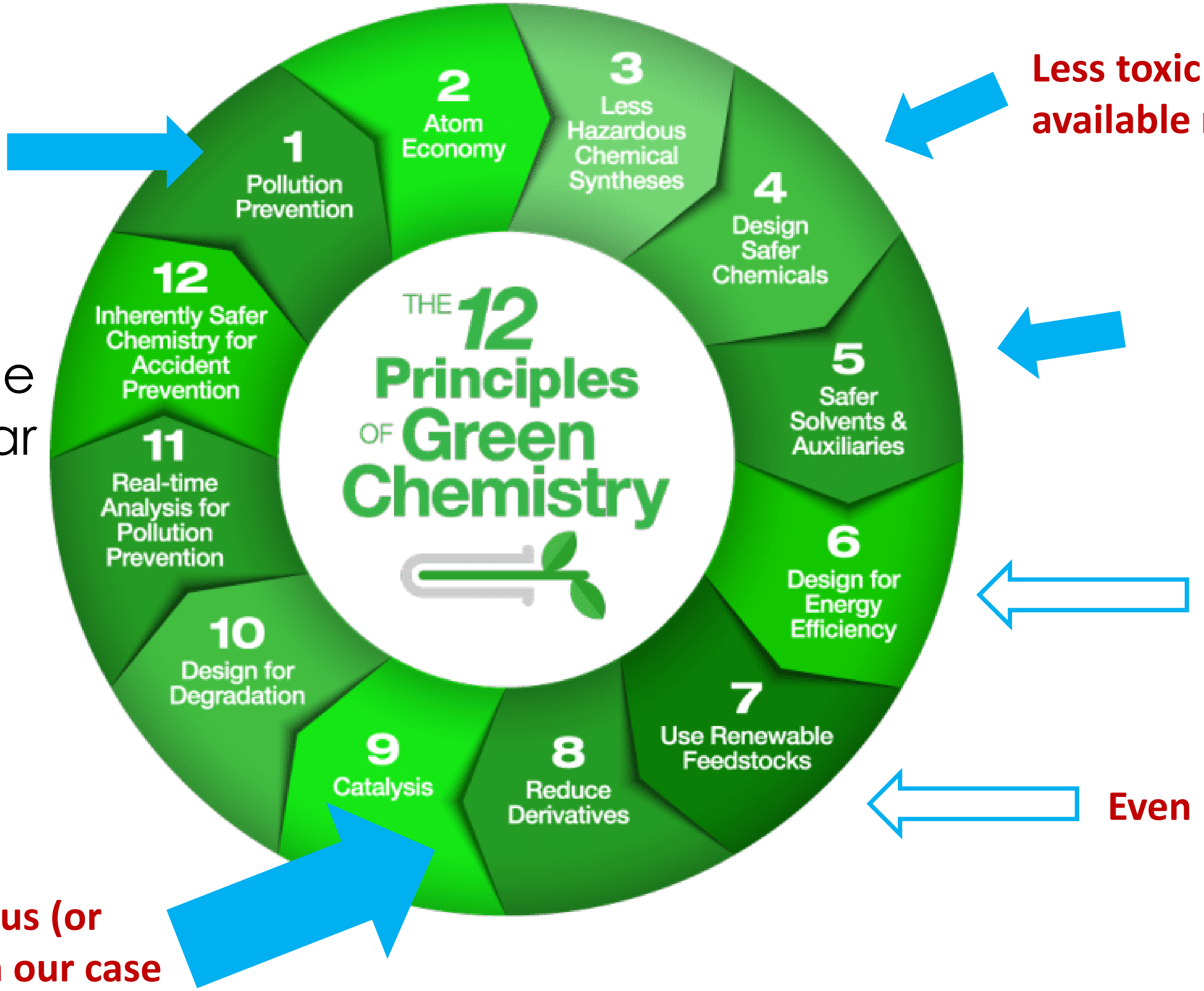
POR FESR EMILIA-ROMAGNA 2014/2020

UNIONE EUROPEA
Fondo europeo di sviluppo regionale

RegioneEmilia-Romagna

Molecular Water Oxidation Catalysis: the second case study

Iron cyclopentadienone complexes as molecular water oxidation electrocatalysts



Less toxic and more available metals

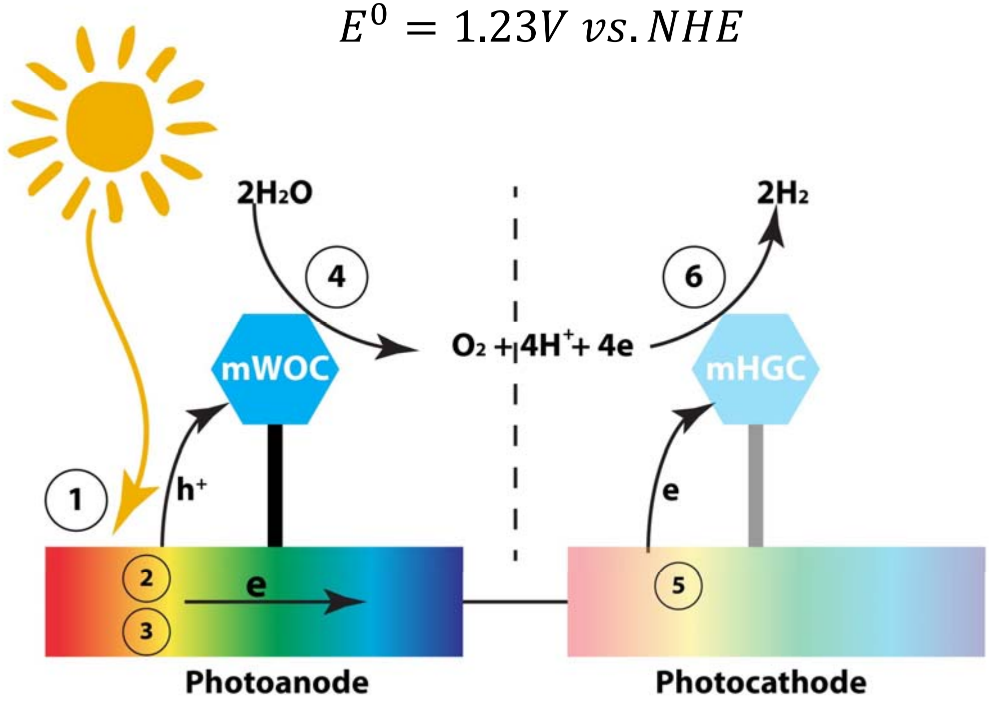
Even better if water

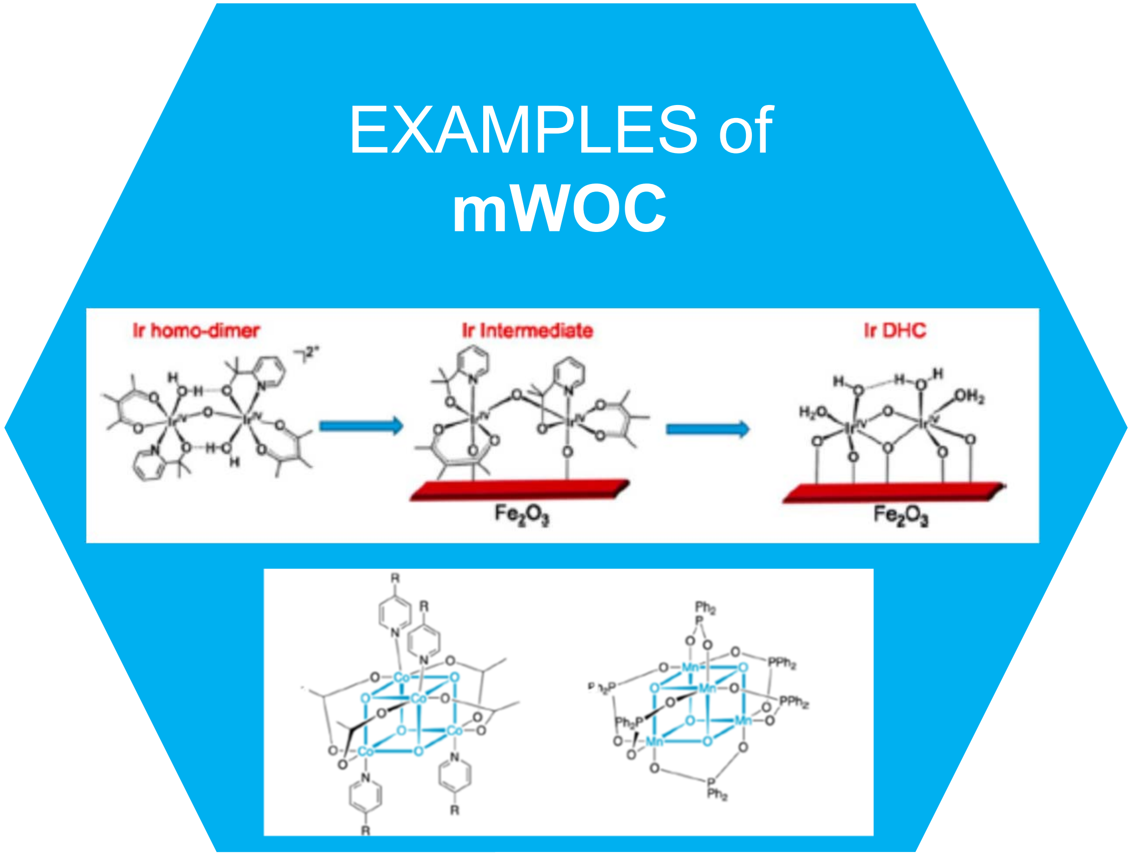
Homogeneous (or «molecular») in our case

The Role of mWOC in Advanced Solar Fuels

Hybrid systems involving molecular catalysts: e.g. Photoelectrochemical H_2 and O_2 production from water

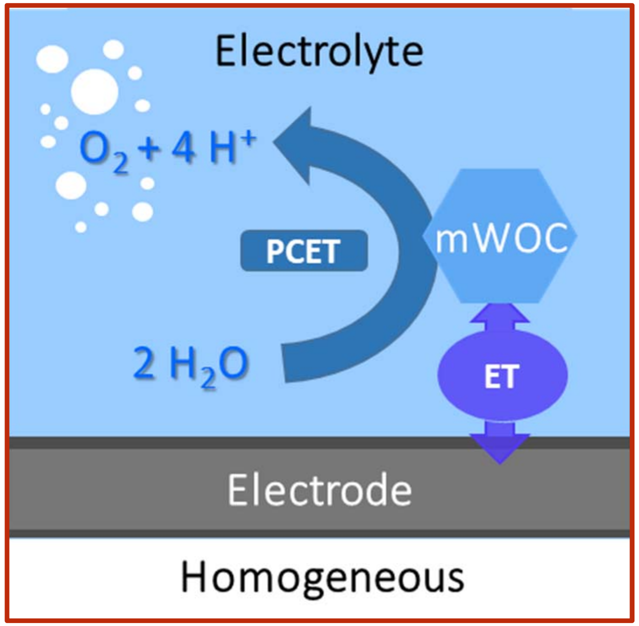
$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
$$E^0 = 1.23V\ vs. NHE$$



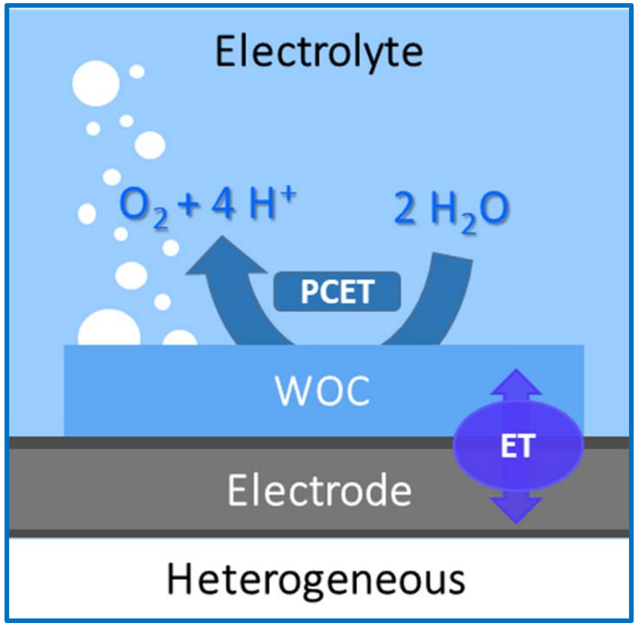


R. H. Crabtree and G. W. Brudvig et al. *ACS Energy Lett., 2020, 5, 3195*

Water Oxidation Catalysis: Homogeneous vs Heterogeneous



Vs.



Advantages

- High efficiency;
- High atom economy;
- Well defined active sites;
- Tunability;
- Mechanistic insights.

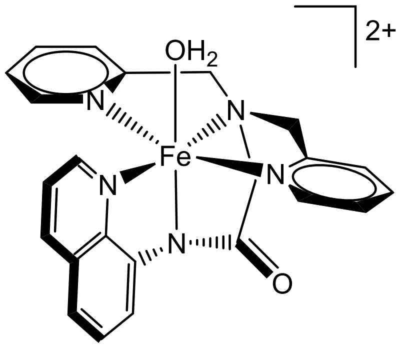
Drawbacks

- High Overpotential;
- Stability:
  - ligand oxidation;
  - ligand loss;
  - dimerization/oligomerization;
  - complex reoganization

Earth Abundant (Fe) Based Molecular mWOC Electrocatalysts

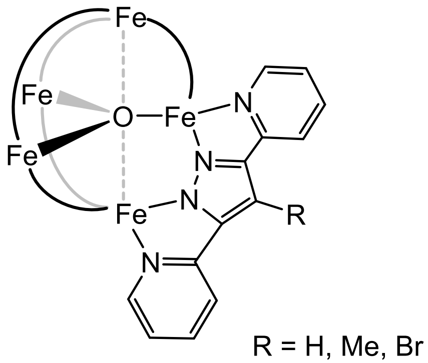
- **Most efficient mWOC**: **noble metals** (e.g. Ru and Ir) based complexes;

- **Fe based mWOC**: state of the art.



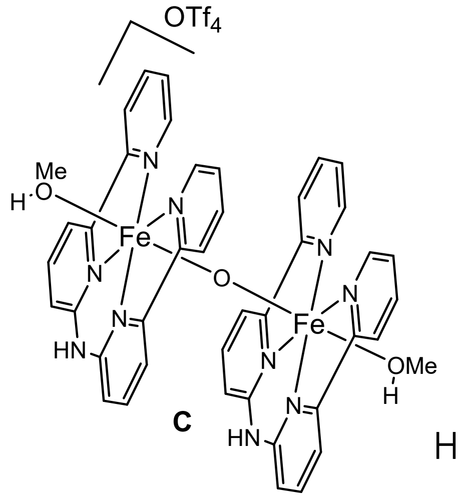
A Meyer

TOF = 0.015 s^{-1}; Overpotential > 0.2-0.25 v



B Masaoka

TOF = 1900 s^{-1}; Overpotential > 0.5 v



C Hetterscheid

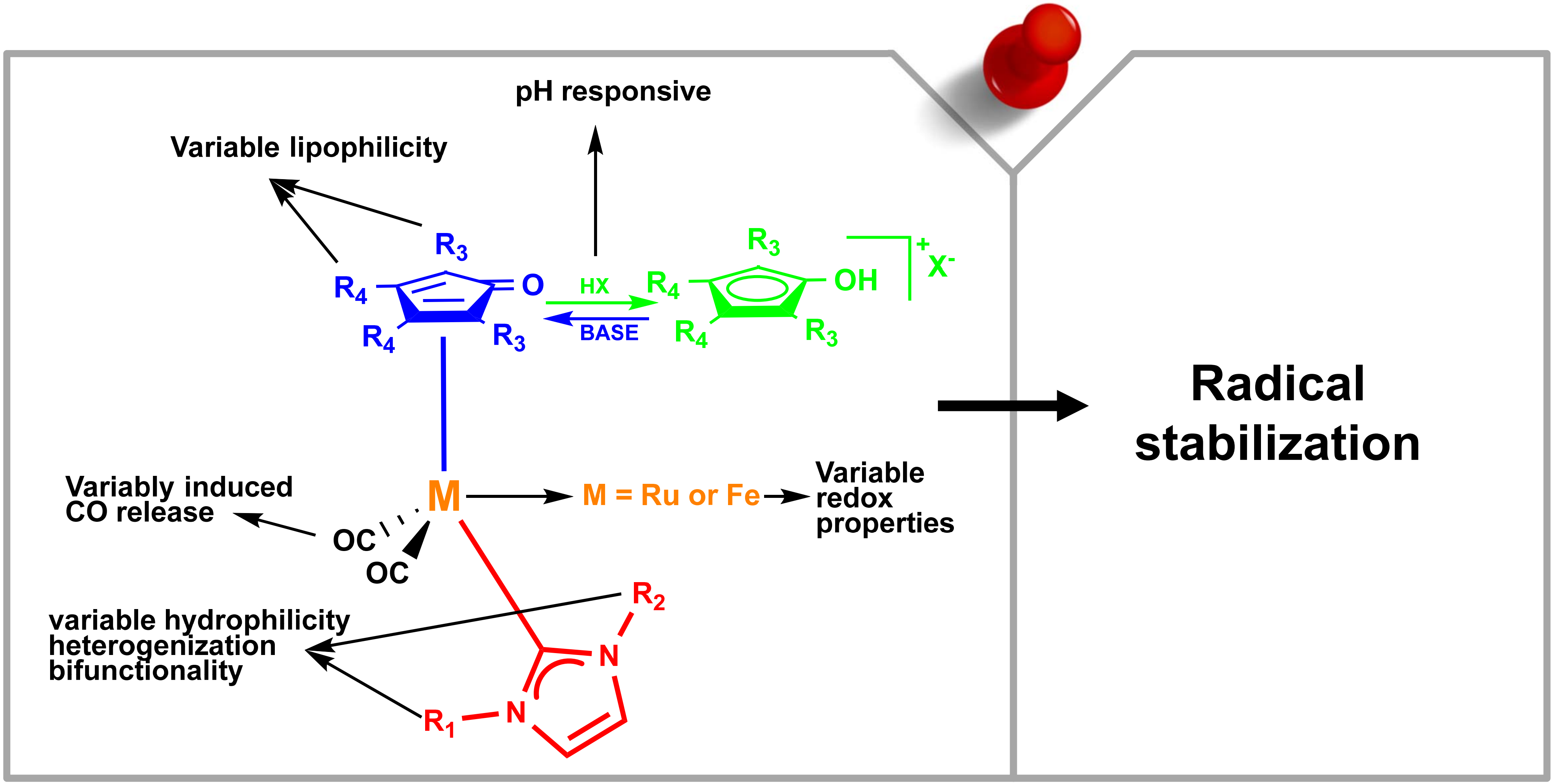
TOF = 0.12 s^{-1}; Overpotential > 0.3-0.4 v

D (Llobet) Found oxidative degradation. Heterogeneous Iron oxide is the real catalyst

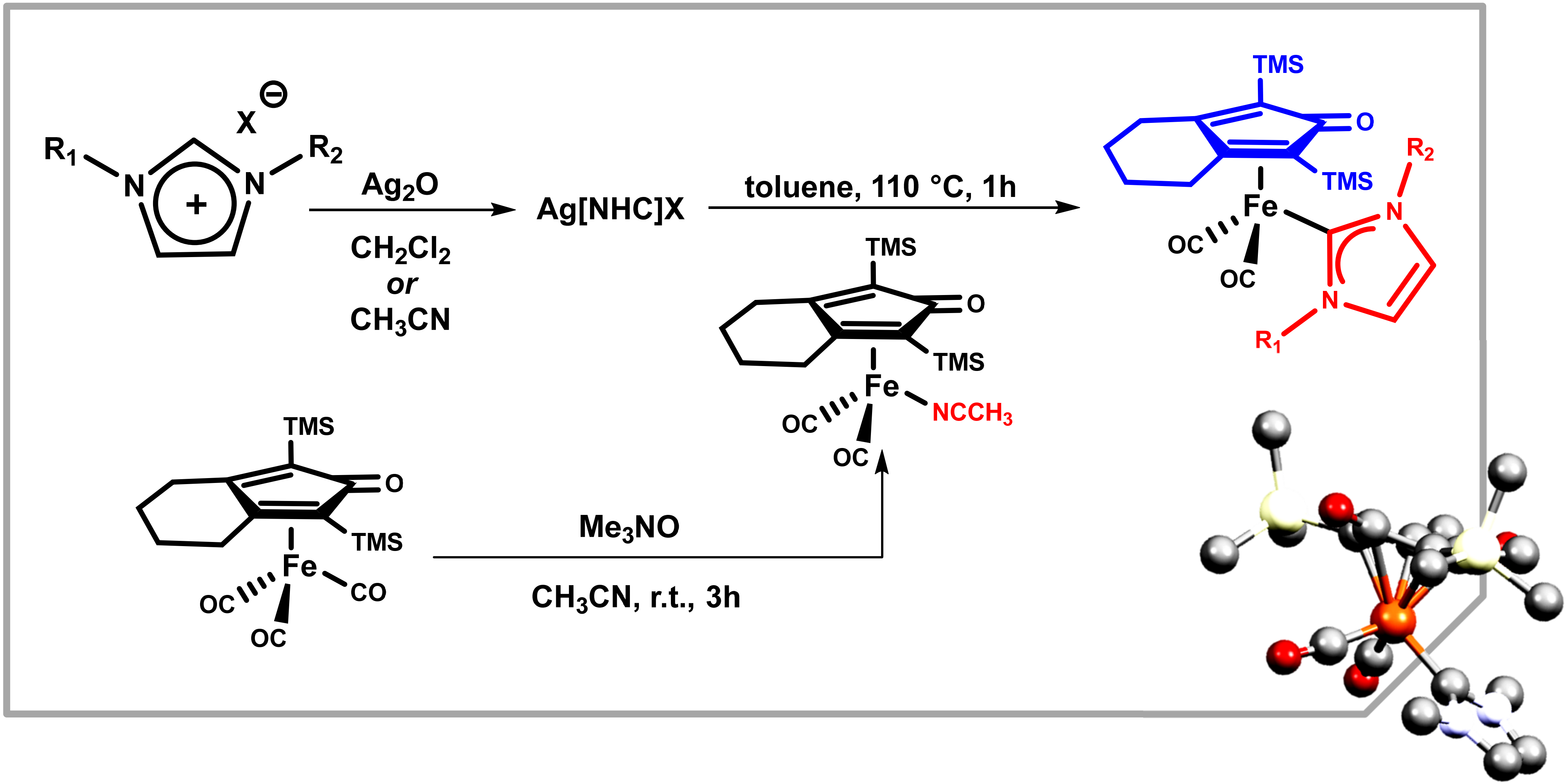
- **Drawbacks**: lower activity, high overpotential; instability.

A) T. J. Meyer, J. Am. Chem. Soc., 2014, 136, 5531–5534. B) S. Masaoka et al., Nature, 2016, 530, 465–468.
C) D. G. Hetterscheid, ACS Catal., 2018, 8, 1052–1061 D) A. Llobet, iScience, 2020, 23, 101378

Cyclopentadienone and N-heterocyclic Carbene
a Powerful Ligands Combination



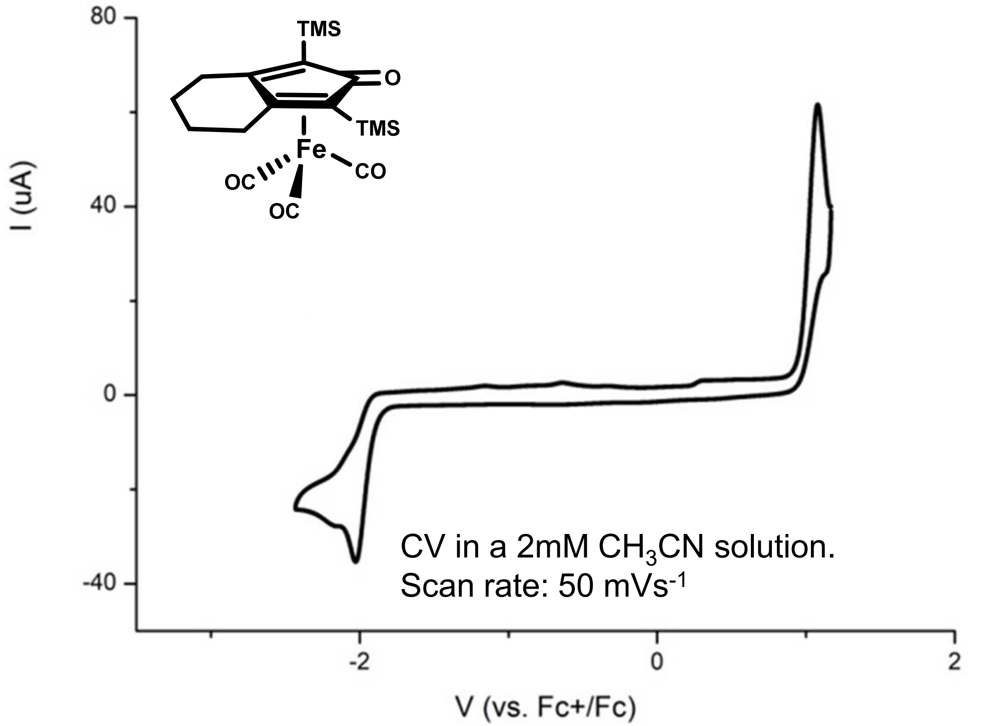
From Ruthenium to Iron: the same easy way of synthesis



A. Cingolani, C. Cesari, S. Zacchini, V. Zanotti, M.C. Cassani, R. Mazzoni, *Dalton Trans.*, ***2015***, *44*, *19063-19067*

Cyclopentadienone-NHC iron(0) Complexes as Water Oxidation Catalysts

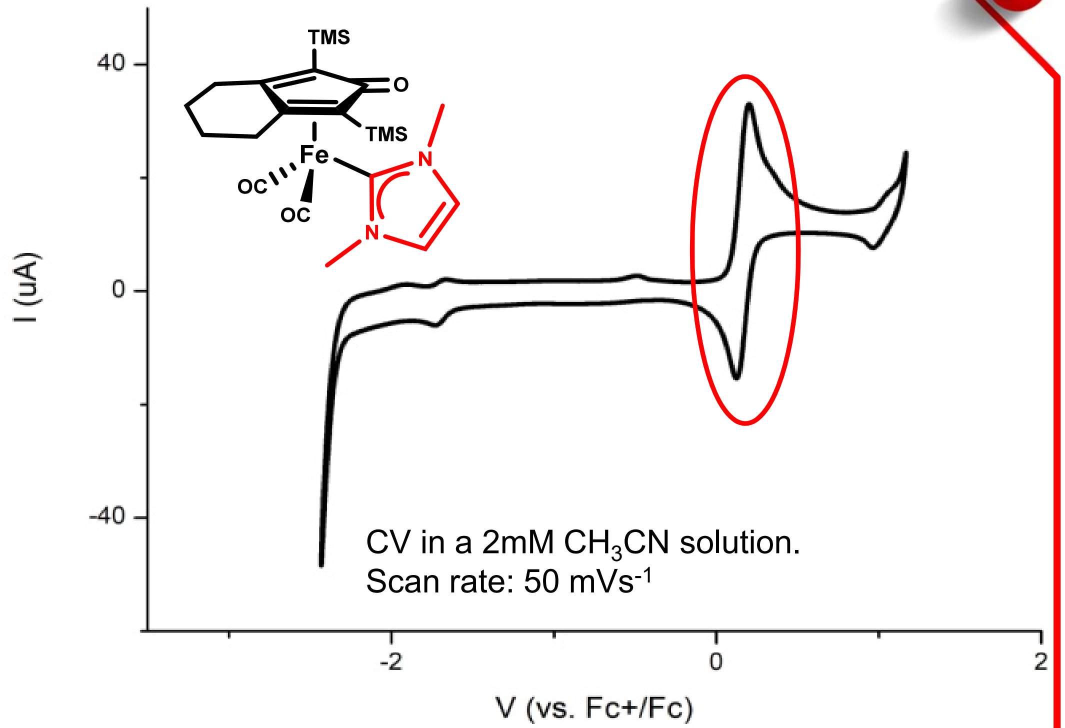
Carbonyl



CV in a 2mM CH_3CN solution.
Scan rate: 50 mVs^{-1}

Vs.

N-heterocyclic carbene



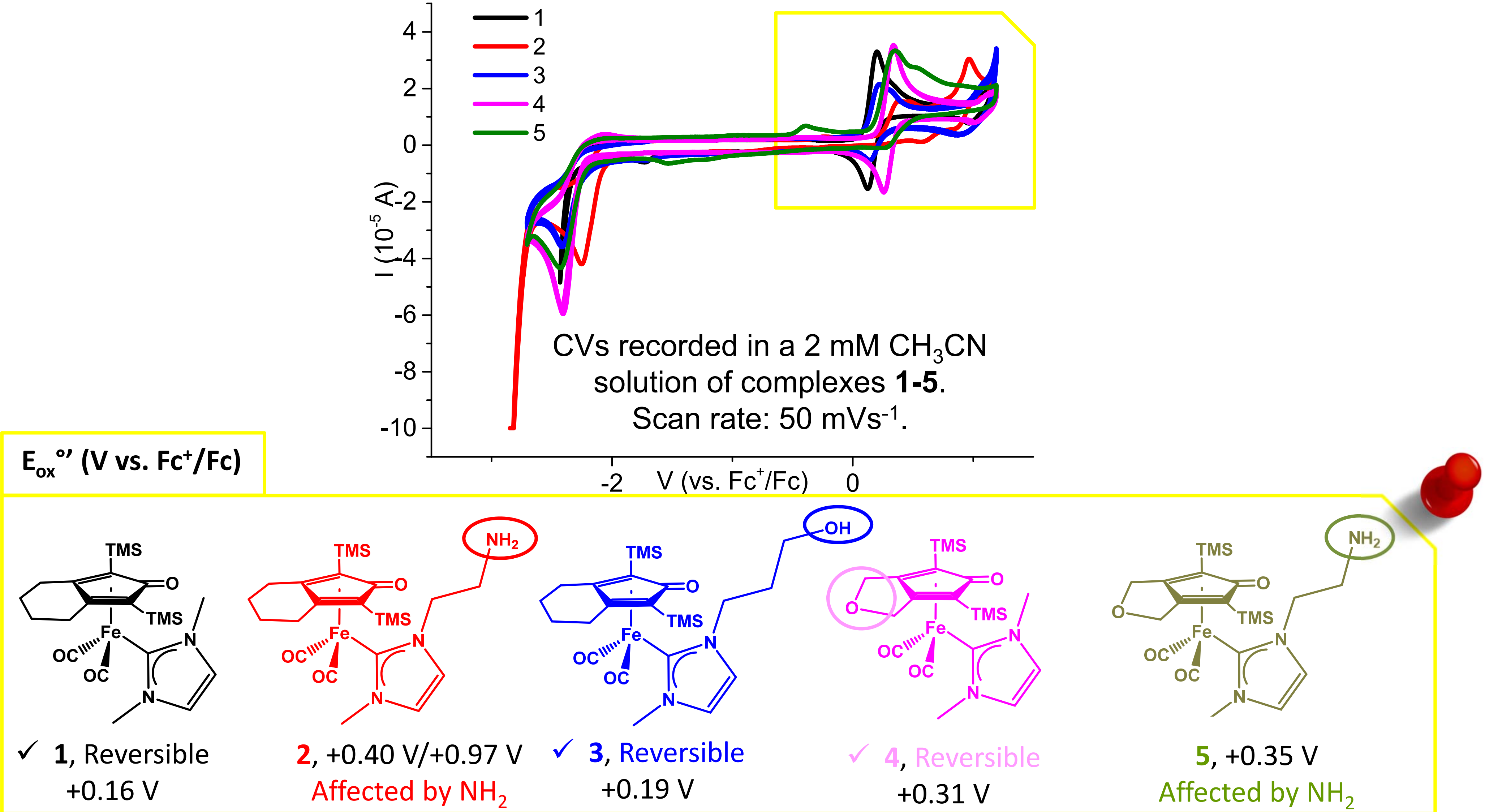
CV in a 2mM CH_3CN solution.
Scan rate: 50 mVs^{-1}

- Irreversible process.

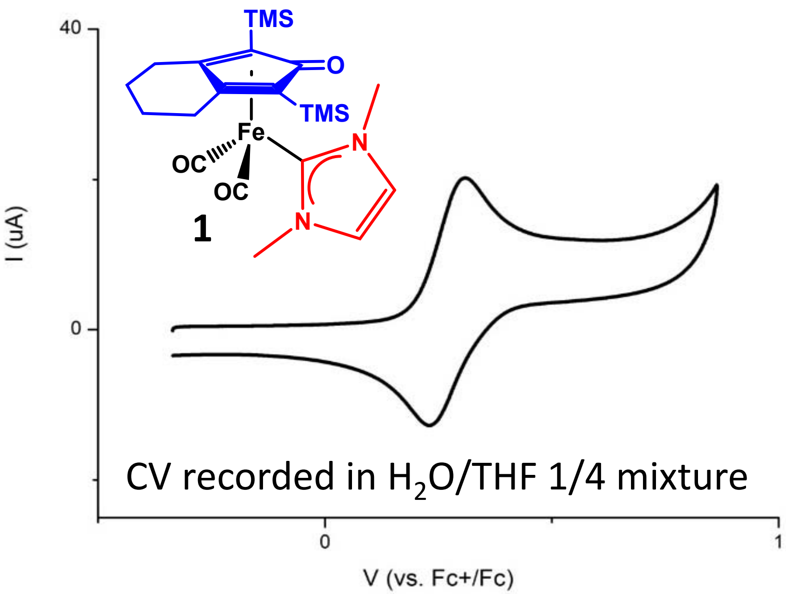
✓ Reversible process at + 0.16 V vs. Fc^+/Fc
✓ O_2/H_2O vs Fc^+/Fc = ca. - 0.2 V in H_2O at pH =14

✓ **NHC shifts the potential towards a region suitable for water oxidation reaction**

The Effect of Ligands Functionalization on Redox Properties



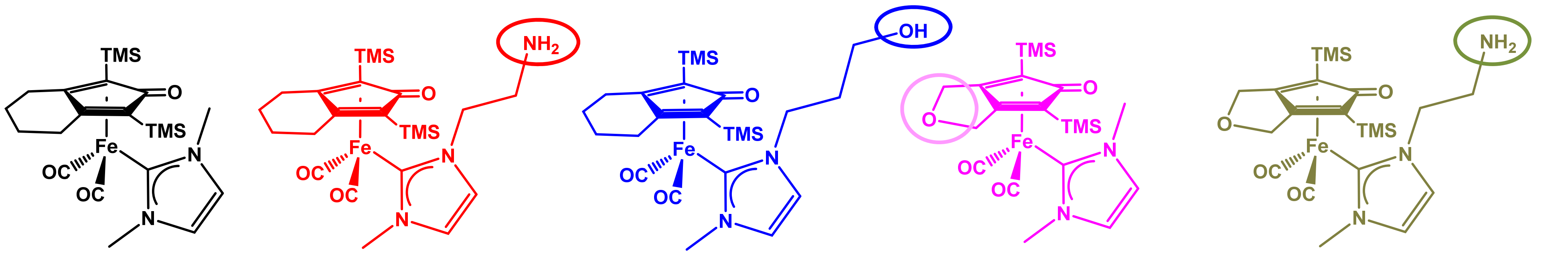
Promising Redox Behaviour is Mantained in H_2O/THF Mixture



CV recorded in H_2O/THF 1/4 mixture

- ✓ Similar CV in H_2O/THF 1/4 mixture
- ✓ Reversible process at + 0.28 - + 0.40 V vs. Fc^+/Fc for **1**, **3** and **4**
- ✓ O_2/H_2O vs Fc^+/Fc = ca. - 0.2 v in H_2O at pH =14

$E_{ox}^{\circ\prime}$ (V vs. Fc^+/Fc)



✓ **1**, Reversible +0.28 V

2, +0.42 V/+0.64 V Affected by NH_2

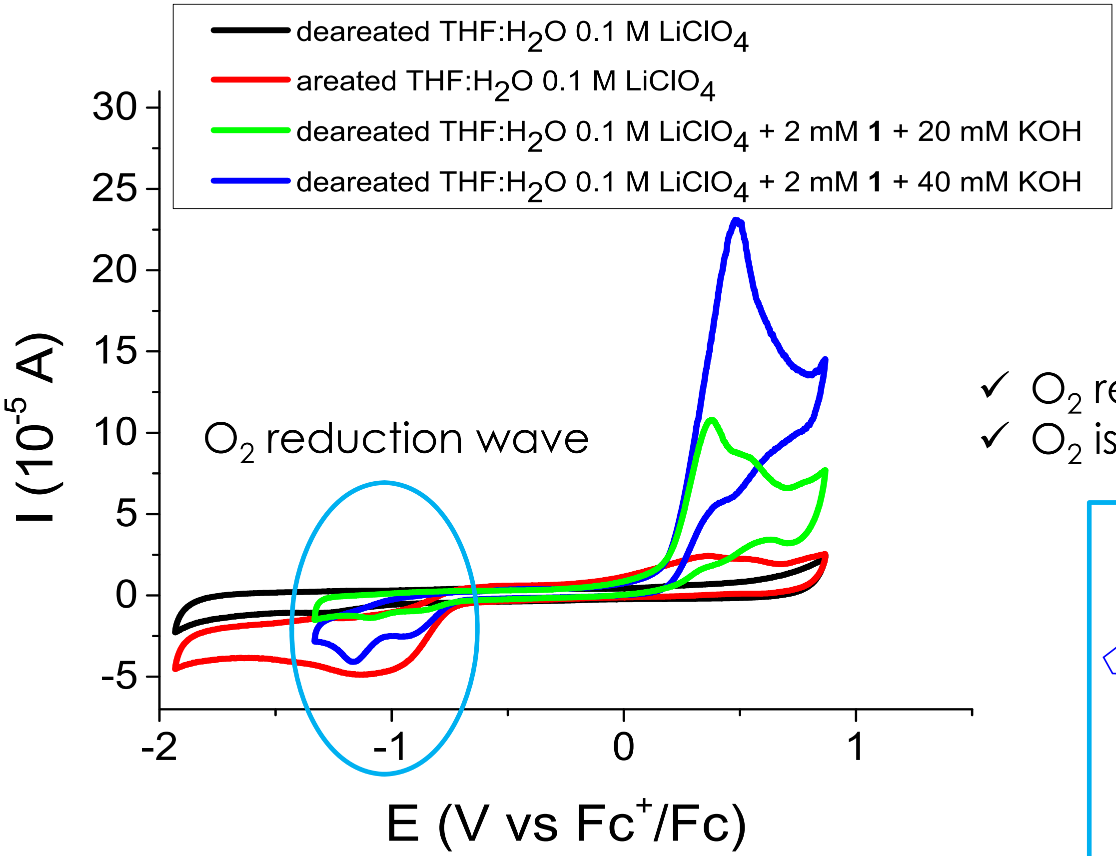
✓ **3**, Reversible +0.29 V

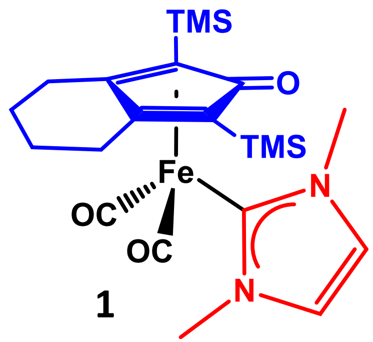
✓ **4**, Reversible +0.40 V

5, +0.50 V Affected by NH_2

Electrocatalysis

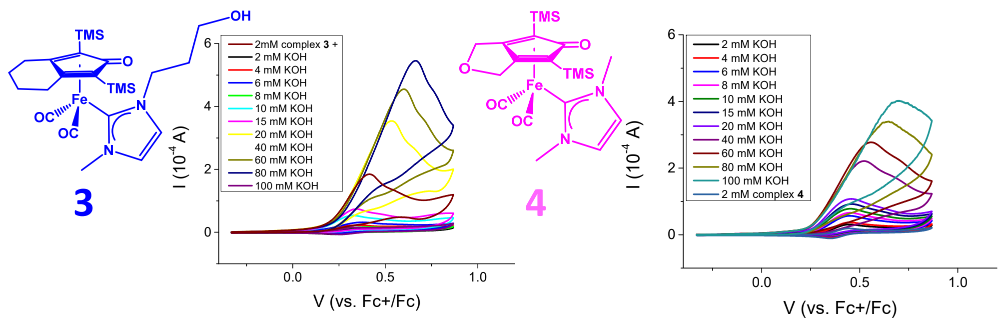
CVs (scan rate = 0.050 V s^{-1}) recorded at a glassy carbon electrode in THF/H_2O solutions **highlights O_2 generated by the electrocatalytic process**.



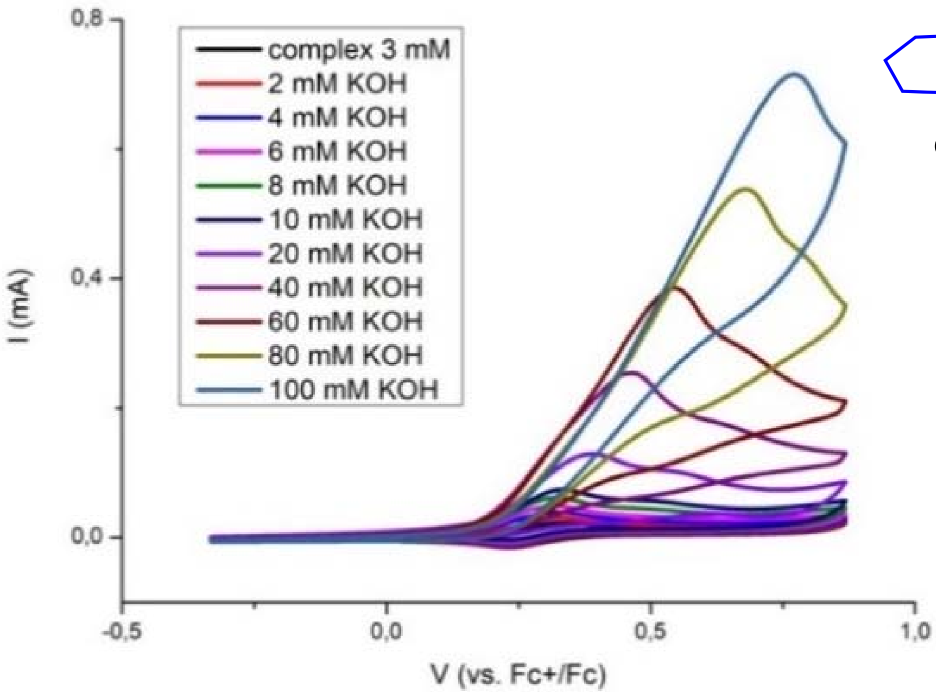


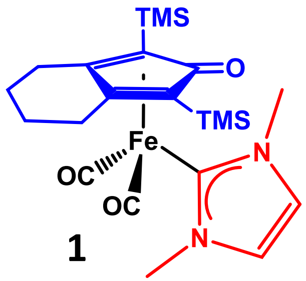
- ✓ O_2 reduction appears in deareated electrolyte;
- ✓ O_2 is produced by electrocatalysis.

- ✓ O-based substituents on cyclopentadienone or NHC

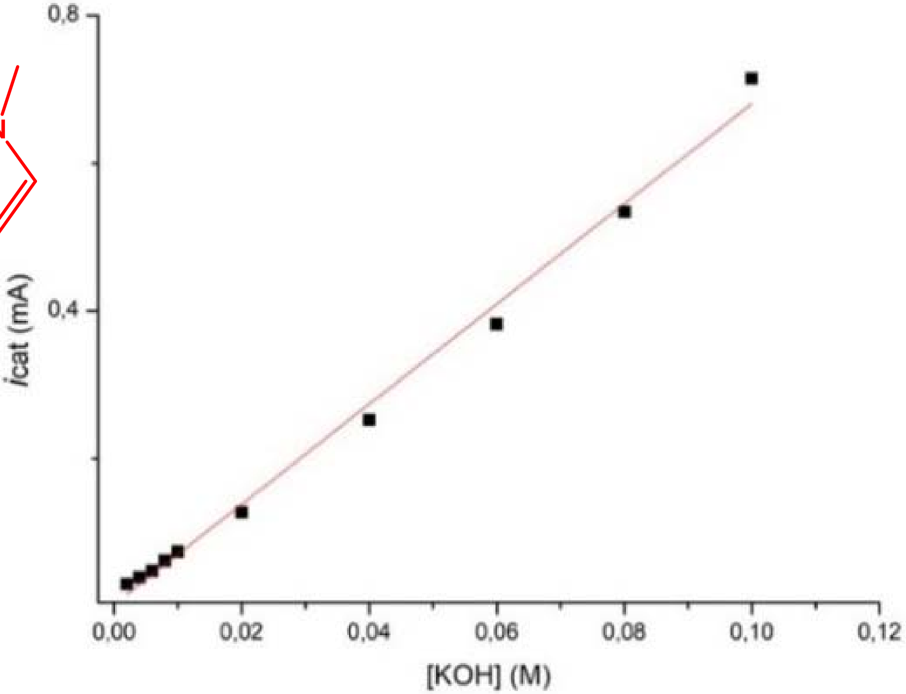


Current increases increasing pH: base dependent mechanism





1



CVs in 3mM solution (THF/H_2O, 4:1) of **1** after subsequent KOH additions. Scan rate: 50 mVs^{-1}.

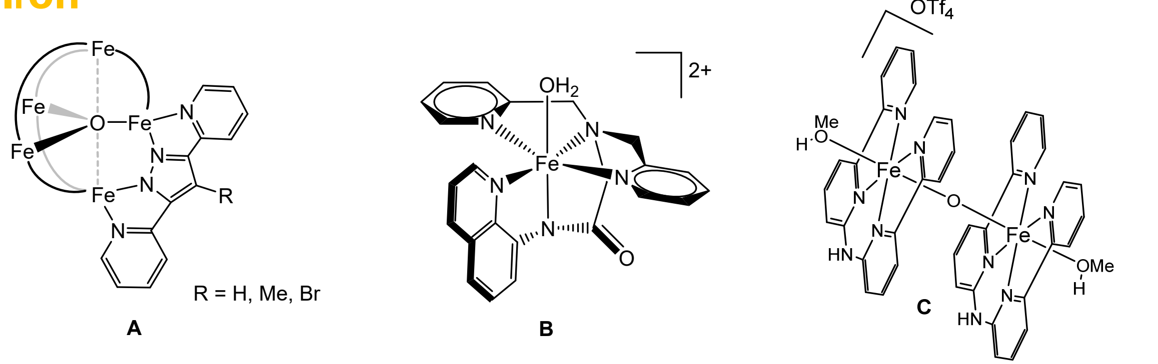
Increasing currents after base addition.

✓ **A stable, effective electrocatalyst for water oxidation in basic H_2O/THF mixture**

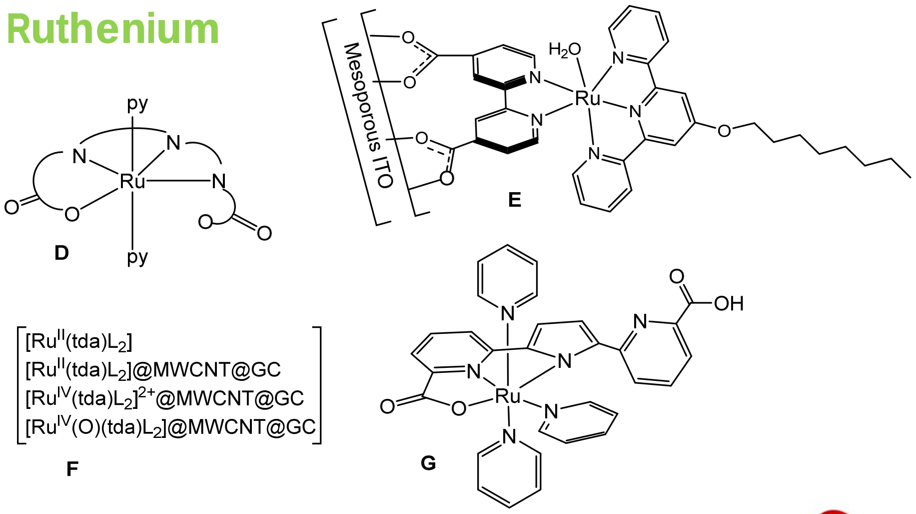
I. Gualandi, R. Mazzoni et al., *Catal. Sci Technol. 2021, 11, 1407-1418*

Efficiency: our catalyst vs. SoA

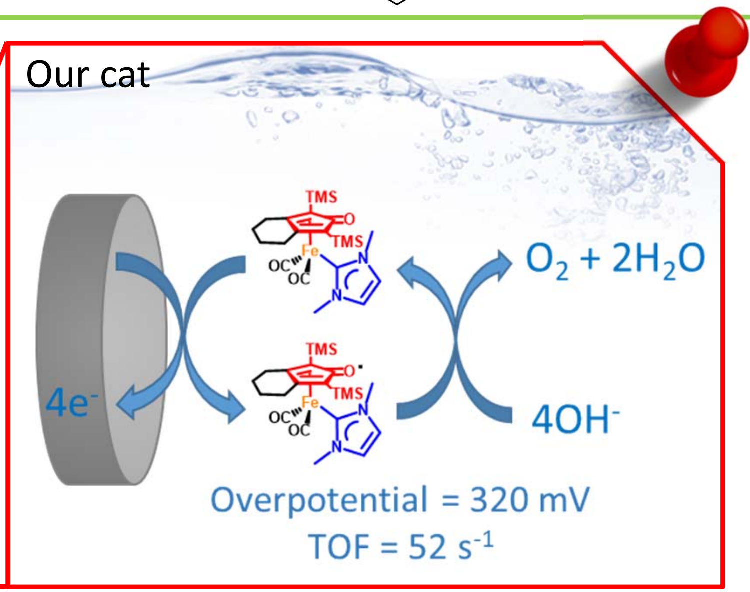
Iron



Ruthenium

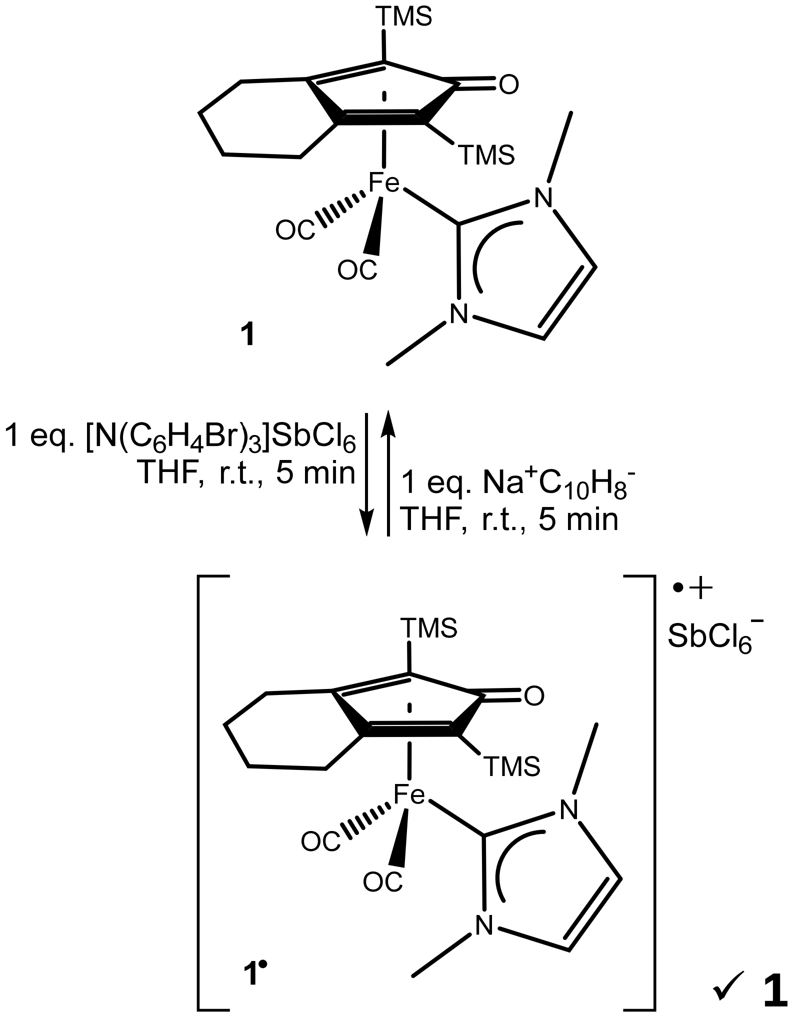


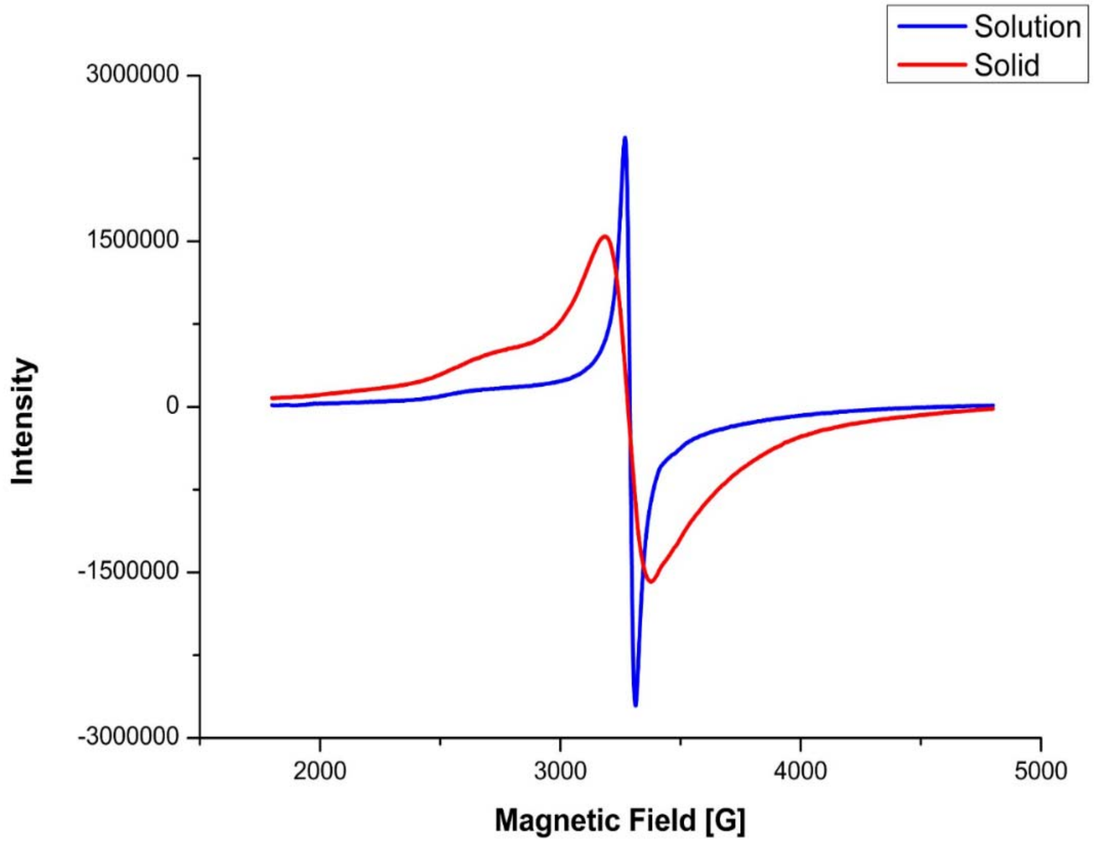
Complex	Electrolyte + Reactant	TOF (s^{-1})	E	Overpotential (V)
A (degradation)	ACN Et_4NClO_4 + Water	1900	1.08 V vs Fc^+/Fc	> 0.5
B	CAN 0.5 $LiClO_4$ + Water	0.015	1.58 V vs NHE	0.2 – 0.25
A (degradation)	ACN TBAP (0.1 M) + Water	300	1.09 V vs Fc^+/Fc	0.65
C	Water Na_2SO_4	0.12	1.75 V vs RHE	0.3 – 0.4
D	pH 7 phosphate buffer	8000	1.43 V vs NHE	0.6
E	0.1 M KNO_3 solution pH 5.9	0.031	1.50 V vs Ag/AgCl	0.41
F	PBS pH 7	8935	1.45 vs NHE	0.634
G	pH 7	9400	1.25 vs NHE	0.434
Our cat	THF:H_2O $LiClO_4$	52	0.28 vs Fc^+/Fc	0.32



A. Cingolani, I. Gualandi, E. Scavetta, C. Cesari, S.Zacchini, D. Tonelli, V. Zanotti, P. Franchi, M. Lucarini, E. Sicilia, G. Mazzone, D. Nanni and R. Mazzoni, *Catal. Sci Technol. 2021, 11, 1407-1418*

Mechanistic Insight: Experimental (a Monoelectronic Process)



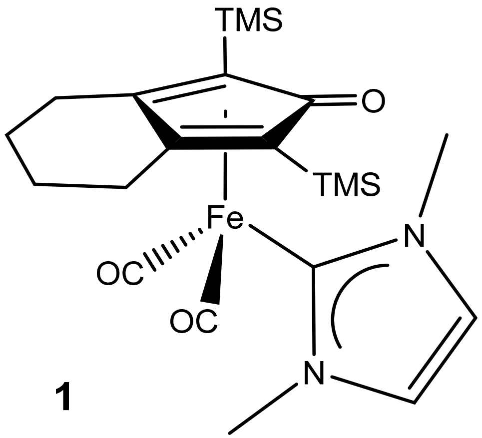


EPR of **1•** in solid (red line) and THF solution (blu line)

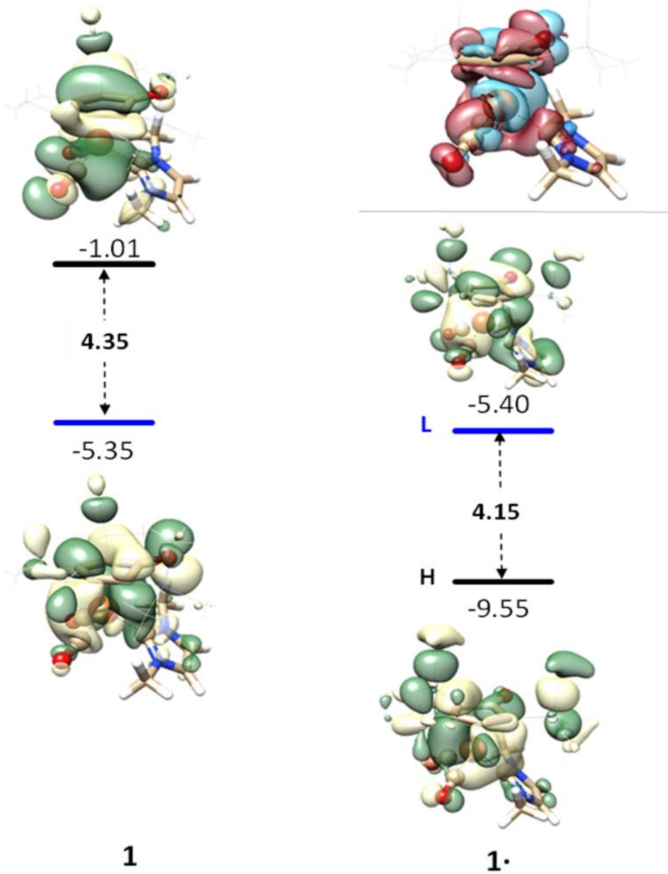
✓ **1•: a very persistent radical cation**

The first step of the cycle: a reversible generation of the radical complex 1•

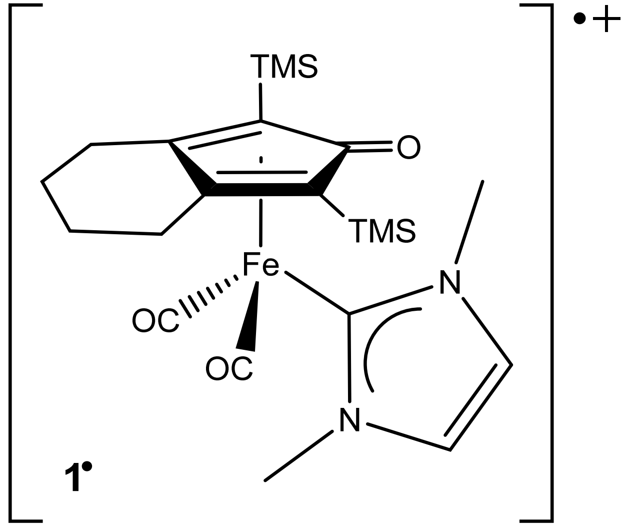
Mechanistic Insight: DFT Calculations
(Frontier Orbitals of 1 and 1˙, and Spin Density of 1˙)



1



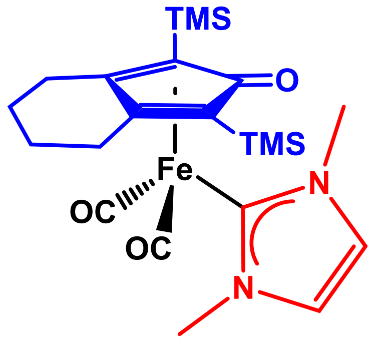
spin density distribution in complex **1˙**
light blue: positive regions;
Purple: negative regions.



1˙

Frontier molecular orbital diagrams HOMO (H) and LUMO (L)
together with the corresponding plots of the orbital surfaces.

Conclusion



- Both ligands play a key role in electrochemistry of the whole system.
- NHC shifts the anodic process in a region suitable for water oxidation;
- Cyclopentadienone favour a monoelectronic redox route as demonstrated by isolation of radical complex **1**$^{\bullet}$ from an exhaustive mono-electronic oxidation;
- Complex **1**, resulted as the best catalyst, is **stable** under WOC conditions and show competitive TOF and overpotential.

Future perspective

- Design new complexes to increase the water solubility of type **1** iron complexes;
- Mechanistic insight by means of EPR characterization (further investigation)
- Immobilization or hybridization toward artificial photosynthetic applications;

ACKNOWLEDGEMENTS

University of Bologna - Department of Industrial Chemistry

- *The lab (synthesis and more)*

Valerio Zanotti
Andrea Cingolani
Cristiana Cesari
Alessandro Messori
Andrea Masetti
Nicola Monti

- *Electrocatalysis*

Isacco Gualandi
Erika Scavetta
Domenica Tonelli

- *X-Ray Diffraction*

Stefano Zacchini

University of Bologna - Department of Chemistry

- *EPR measures (Unibo – Department of Chemistry)*

Paola Franchi
Marco Lucarini

University of Calabria - Department of Chemistry and Chemical Technologies

- *DFT calculation (University of Calabria)*

Emilia Sicilia
Gloria Mazzone

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Who really work, me aside… a picture from yesterday lab

Above all,
Thanks to them

Immediately after…

Thank you! for your kind attention

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