TECHNISCHE UNIVERSITÄT DRESDEN

DRESDEN concept

Edelmetallfreie und nachhaltige Katalyse in der Organischen Synthese
(Noble metal-free and Sustainable Catalysis in Organic Synthesis)

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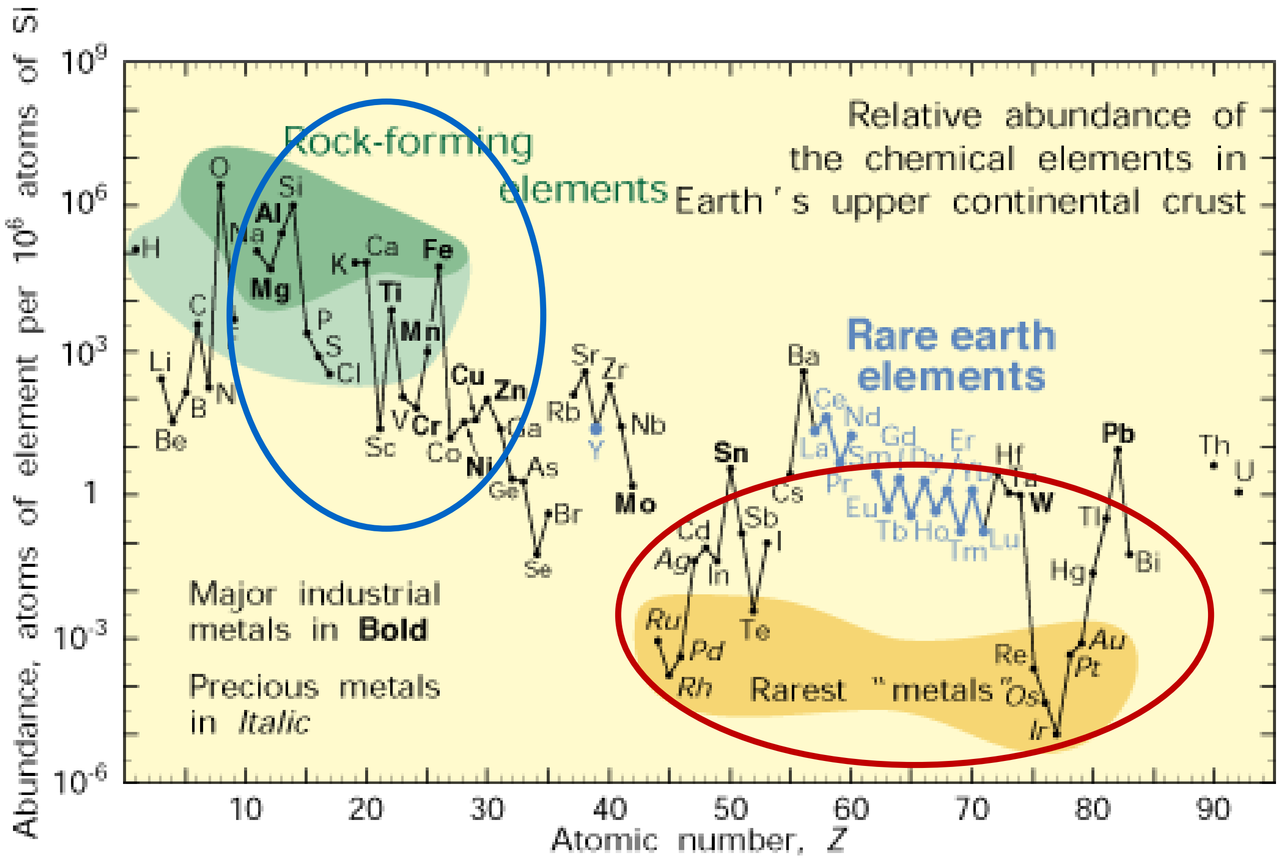
Motivation

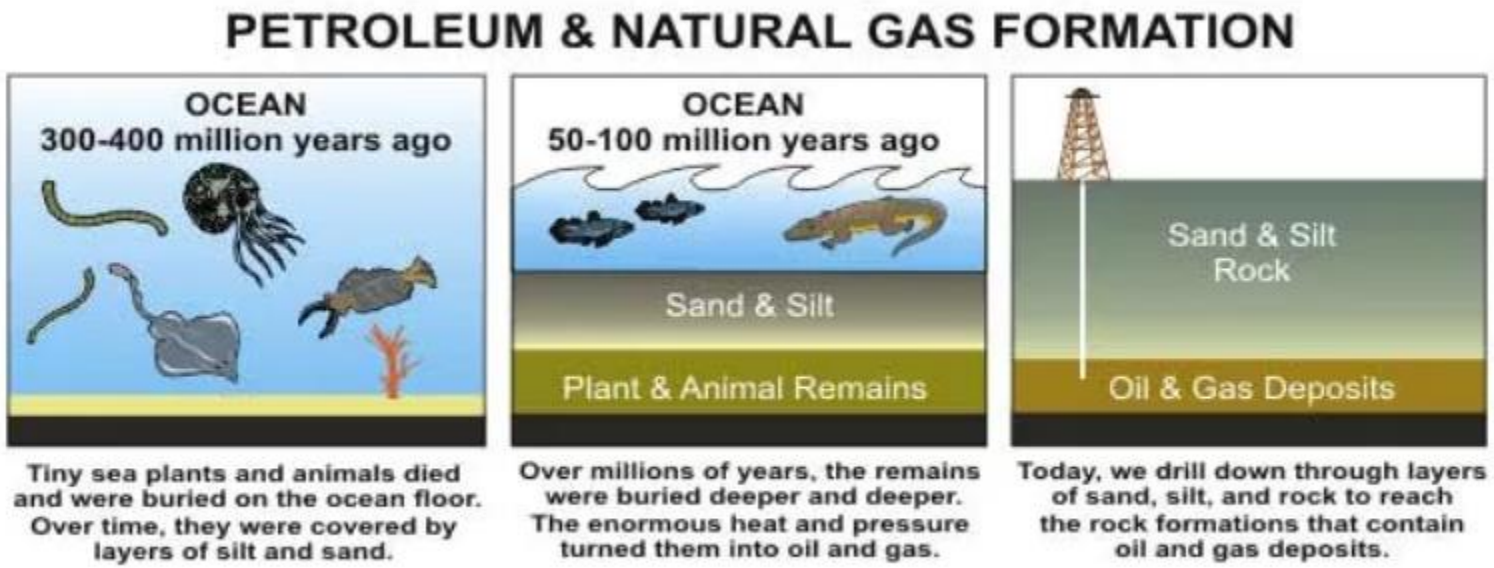
- **Catalysis** is an enabling technology for a sustainable future (chemical) process development.
- The majority of process however rely on the use of **precious metal-based catalysts**.
- These metals are not found in the upper earth crust.
- **Earth-abundant metal-catalysis** could offer a solution, but needs to be reinvented



Picture taken from https://pubs.usgs.gov/fs/2002/fs087-02/

Inspiration by Nature – The Secrets of Methanobacter (or the biosynthesis of coal)

How we learn the synthesis of fuels in school:



Tiny sea plants and animals died and were buried on the ocean floor. Over time, they were covered by layers of silt and sand.

Over millions of years, the remains were buried deeper and deeper. The enormous heat and pressure turned them into oil and gas.

Today, we drill down through layers of sand, silt, and rock to reach the rock formations that contain oil and gas deposits.

The generally accepted theory for the origin of petroleum a geologic processing of the dead remains of ancient ocean life. (Image credit: DOE)

But how did this happen?

Organisms contain
- **proteins,**
- **carbohydrates,**
- **lipids**

while:

coal, oil and gas are lacking oxygen, or nitrogen

Two different decomposition pathways are operative: the aerobic and anaerobic pathway

Inspiration by Nature – The Secrets of Methanobacter (or the biosynthesis of coal)

The aerobic pathway...

$C_6H_2O_2 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O + \text{energy}$

carbohydrates

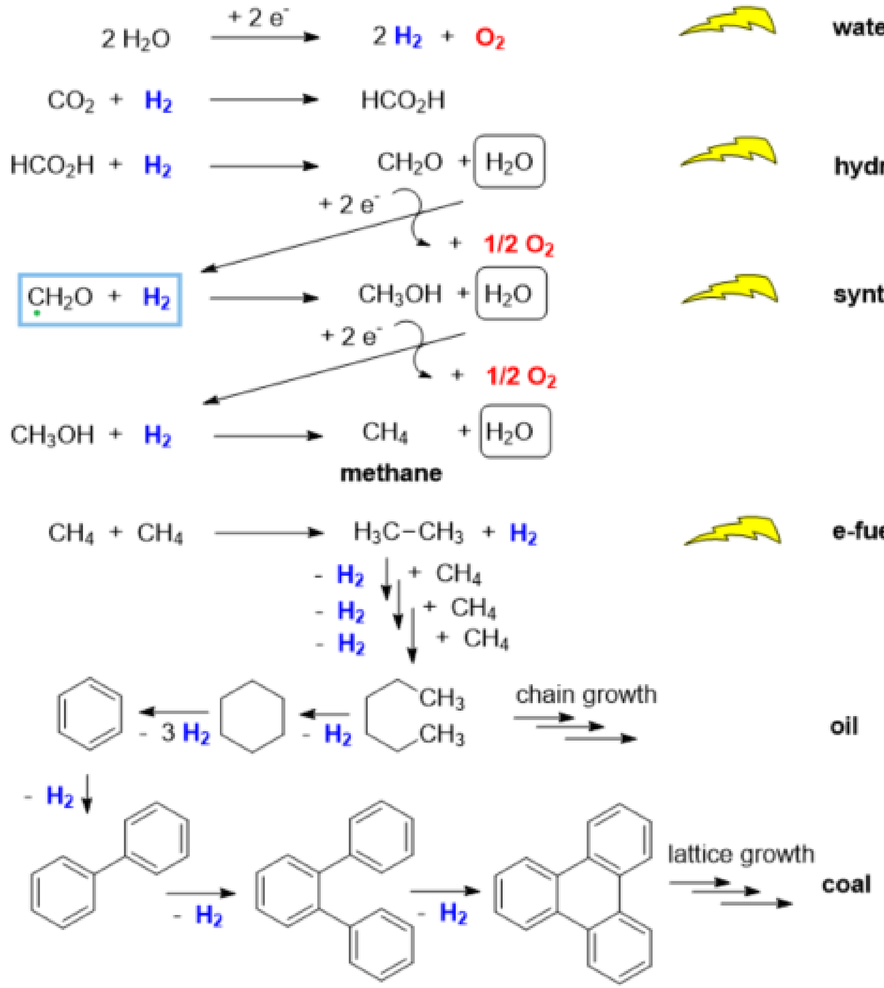
lipids

amino acids

aromatics

...results in an accumulation of CO_2

The anaerobic pathway... or: How to get oxygen?



$2\,H_2O \xrightarrow{+2\,e^-} 2\,H_2 + O_2$

$CO_2 + H_2 \longrightarrow HCO_2H$

$HCO_2H + H_2 \longrightarrow CH_2O + \boxed{H_2O}$

$+2\,e^-$ $+ 1/2\,O_2$

$\boxed{CH_2O + H_2} \longrightarrow CH_3OH + \boxed{H_2O}$

$+2\,e^-$ $+ 1/2\,O_2$

$CH_3OH + H_2 \longrightarrow CH_4 + \boxed{H_2O}$

methane

$CH_4 + CH_4 \longrightarrow H_3C{-}CH_3 + H_2$

water splitting

hydrogen storage

synthetic building blocks

e-fuels (power2X)

oil

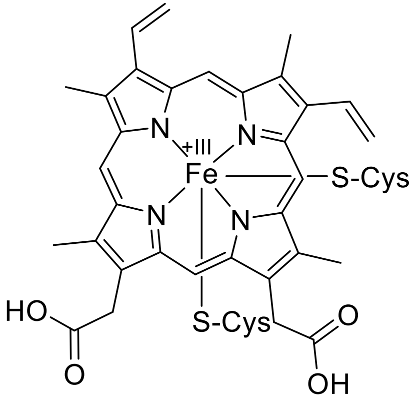
coal

Important:

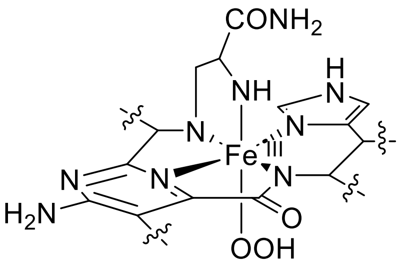
Fe-containing enzymes are involved in every process

Iron-complexes in enzymes – a selection

oxygen transfer



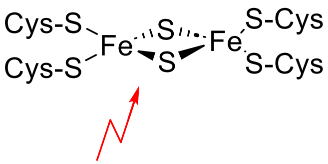
hem-Fe-complexes
e.g. cytochrome P450



non-hem-Fe-complexes
e.g. Rieske-monooxygenase

electron transfer

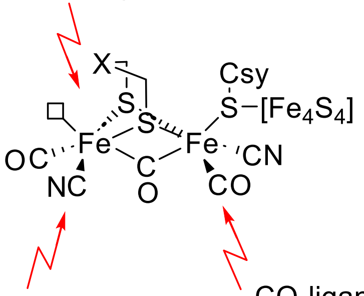
Fe-S-cluster
z.B. Ferredoxin



S-ligand
-redox active

[FeFe]-hydrogenase

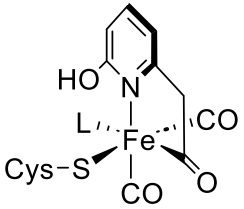
oxidation state of the Fe-center
depends on the ligand



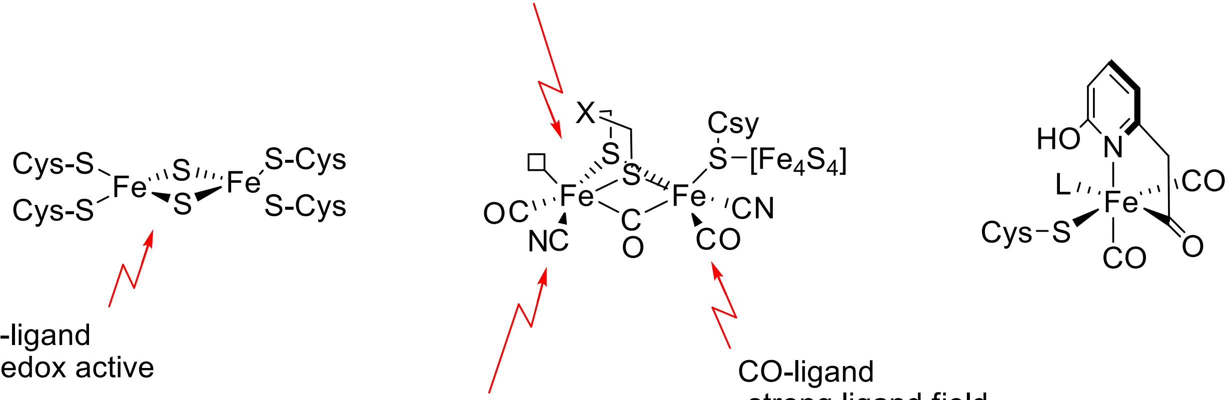
cyanide ligand
-redox-active

CO-ligand
-strong ligand field
-diamagnetic complex

[Fe]-hydrogenase



Characteristics of Fe-containing electron transfer proteins



oxidation state of the Fe-center
depends on the ligand

S-ligand
-redox active

cyanide ligand
-redox-active

CO-ligand
-strong ligand field
-diamagnetic complex

- -

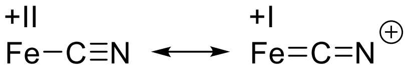
"Redox-active, or 'noninnocent,' ligands have more energetically accessible levels that allow redox reactions to change their charge state."

P. Chirik, K. Wieghardt *Science*, **2010**, *327*, 794.

"Oftentimes, the two descriptions 'redox-active' and 'noninnocent' ligands are used interchangeably in the literature. However, care must be used when using the latter because clearly defined physical oxidation states have often been established for a case where ambivalence has been implied."

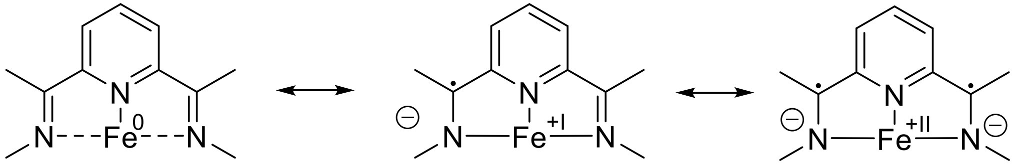
P. Chirik *J. Inorg. Chem.*, **2011**, *50*, 9737.

Redox-active („non-innocent“) ligands are key to catalytic activity



$$\overset{+II}{Fe}-C\equiv N \longleftrightarrow \overset{+I}{Fe}=C=N^{\oplus}$$

Wieghardt / Chirik / deBeer

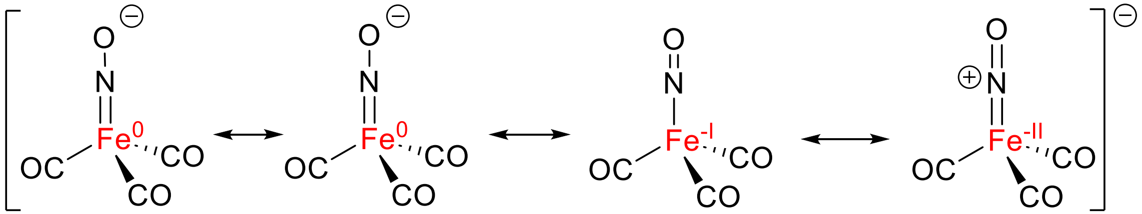


catalysis by means of
- single-electron oxidation of the metal

plus

- single-electron oxidation of the ligand

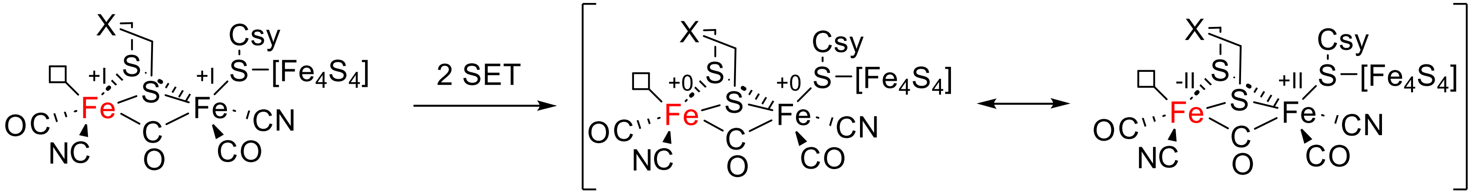
⇨ ***ligand-metal cooperativity is a key***



$\{^3Fe(^3NO)\}^{10}$ $\{^1Fe(^1NO)\}^{10}$

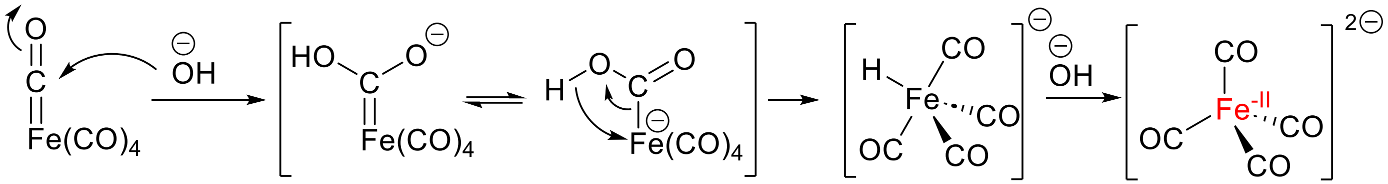
NO-Ligand is redox-active!!

Redox-active („non-innocent“) ligands are key to catalytic activity



Hieber base reaction

1928

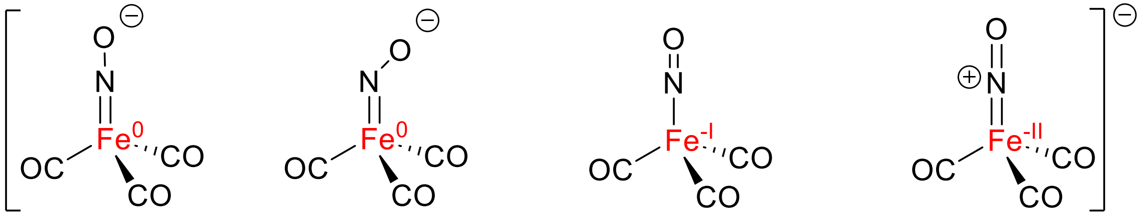


catalytically inactive

1963

$$Fe(CO)_5 + NaNO_2 \longrightarrow Na[Fe(CO)_3(NO)] + CO_2 + CO$$

catalytically active

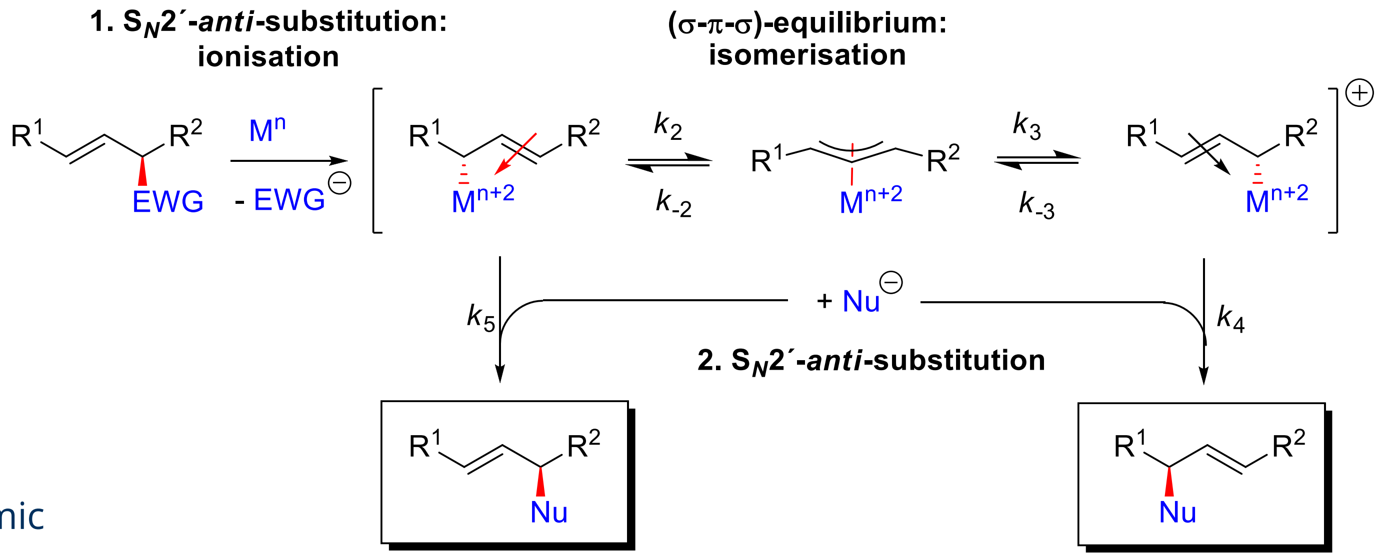


$\{^3Fe(^3NO)\}^{10}$ $\{^1Fe(^1NO)\}^{10}$

Low-valent carbonylferrates as elektronentransfercatalysts?

Case 1: The Fe-catalyzed allylic substitution **Tsuji-Trost reaction**

Mechanism:



Common catalysts:

Pd-, Ir-, W-, Mo-complexes

Pro:

DYKAT-mechanism

-> highly enantioselective transformation of racemic starting material

Contra:

Formation of regioisomers

Low-valent carbonylferrates as elektronentransfercatalysts?

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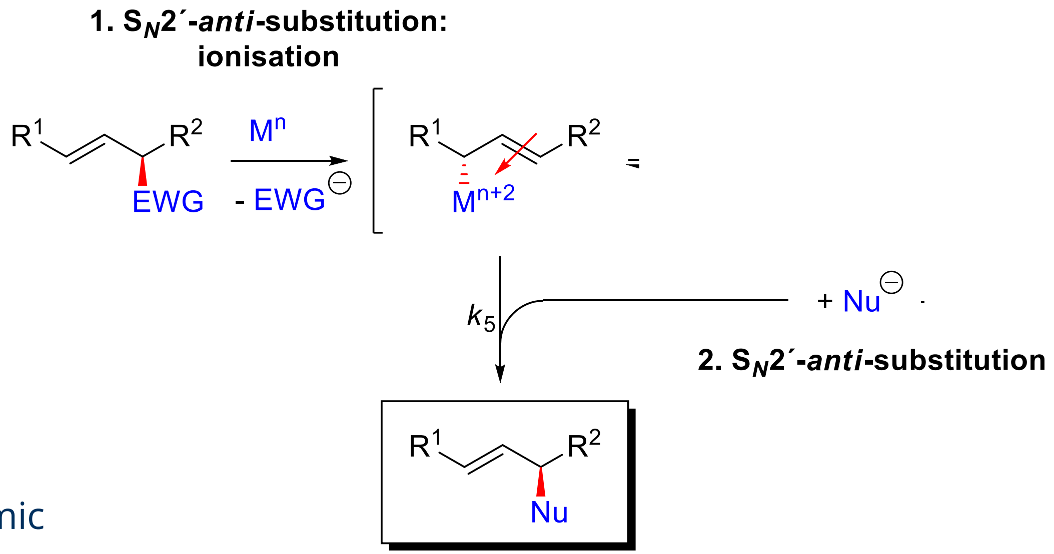

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Pro:

DYKAT-mechanism

-> highly enantioselective
transformation of racemic
starting material

Contra:

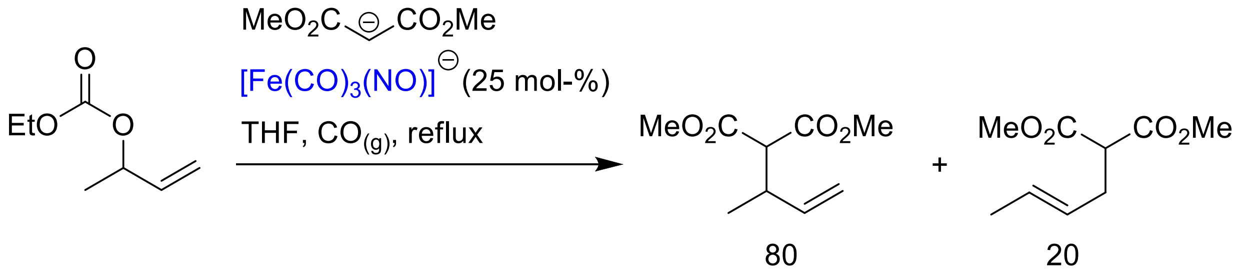
Formation of regioisomers

Potential catalyst for regioselective allylic substitutions:

coordinatively oversaturated, nucleophilic metal complex

Review: *Eur. J. Org. Chem.* 2009, *775*.

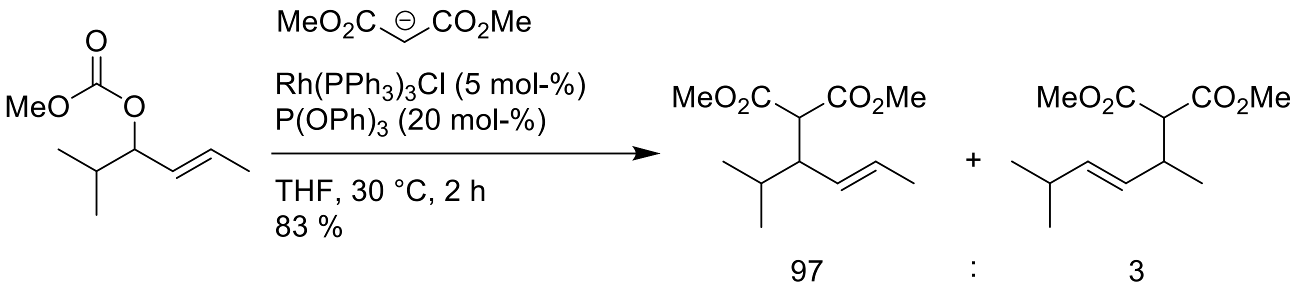
Case 1: The Fe-catalyzed Tsuji-Trost allylation



	cation	*yield (%)*
Roustan (1979):	$Na^{\oplus}$	85
Zhou (1987):	$Bu_4N^{\oplus}$	35

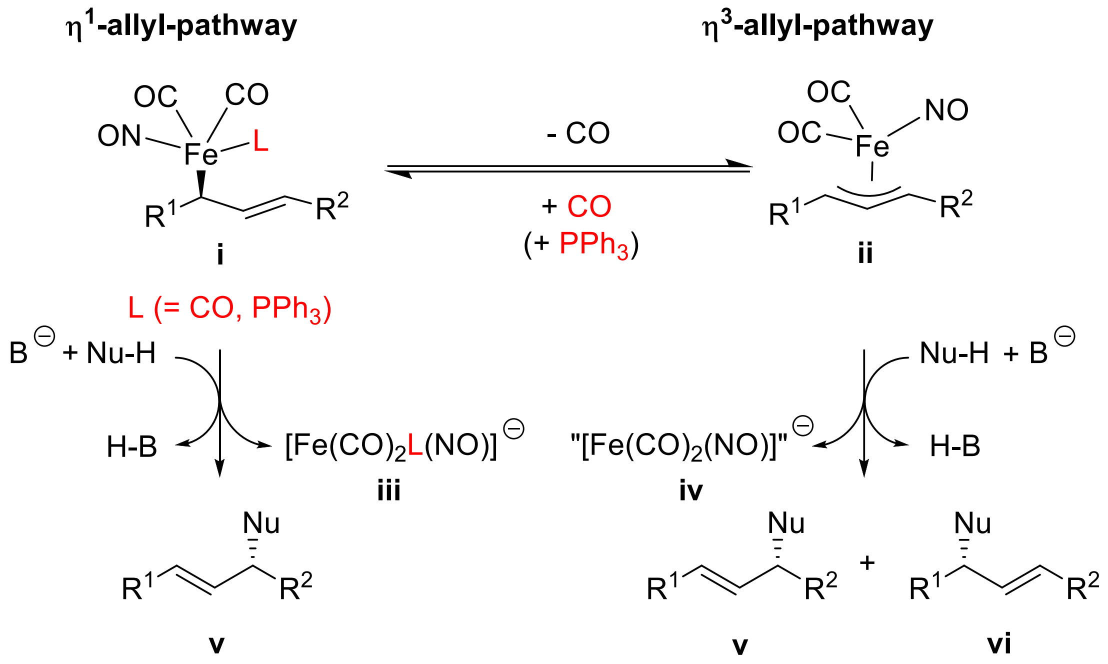
State of research

Evans (1998):



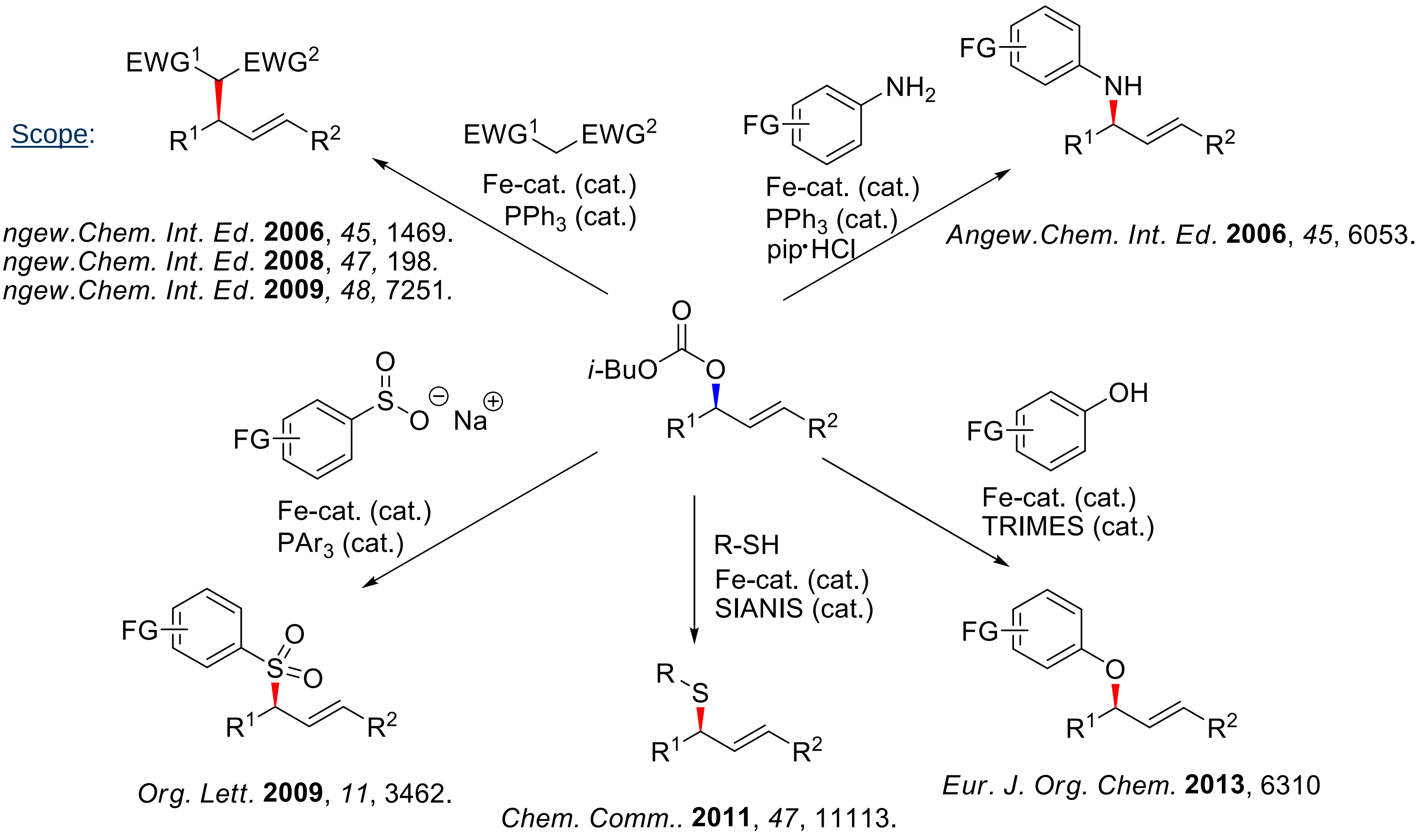
Case 1: The Fe-catalyzed Tsuji-Trost allylation

Working hypothesis



Review: *Eur. J. Org. Chem.* 2009, *775.*

Case 1: The Fe-catalyzed Tsuji-Trost allylation



Scope:

EWG^1 EWG^2
Fe-cat. (cat.)
PPh$_3$ (cat.)

Angew.Chem. Int. Ed. **2006**, *45*, 1469.
Angew.Chem. Int. Ed. **2008**, *47*, 198.
Angew.Chem. Int. Ed. **2009**, *48*, 7251.

Fe-cat. (cat.)
PPh$_3$ (cat.)
pip·HCl

Angew.Chem. Int. Ed. **2006**, *45*, 6053.

Fe-cat. (cat.)
PAr$_3$ (cat.)

R-SH
Fe-cat. (cat.)
SIANIS (cat.)

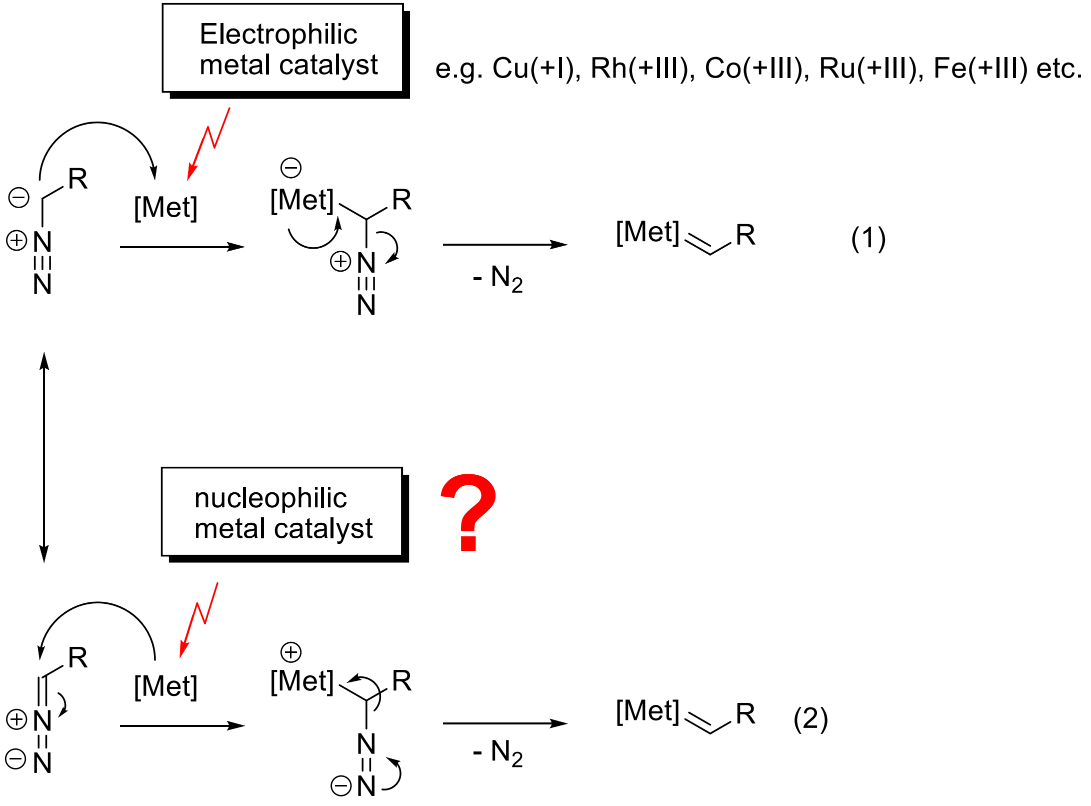
Fe-cat. (cat.)
TRIMES (cat.)

Org. Lett. **2009**, *11*, 3462.

Chem. Comm.. **2011**, *47*, 11113.

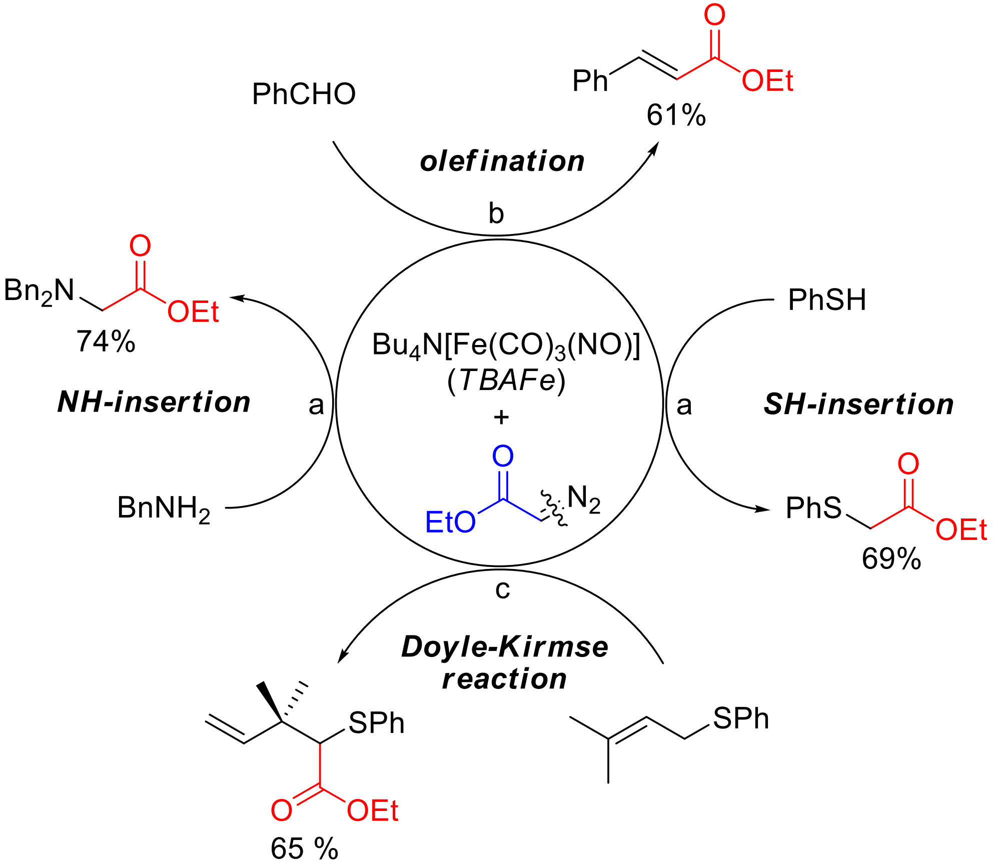
Eur. J. Org. Chem. **2013**, 6310

Case 2: Fe-catalyzed carbene transfer reactions



ACIE **2012**, *51*, 5351

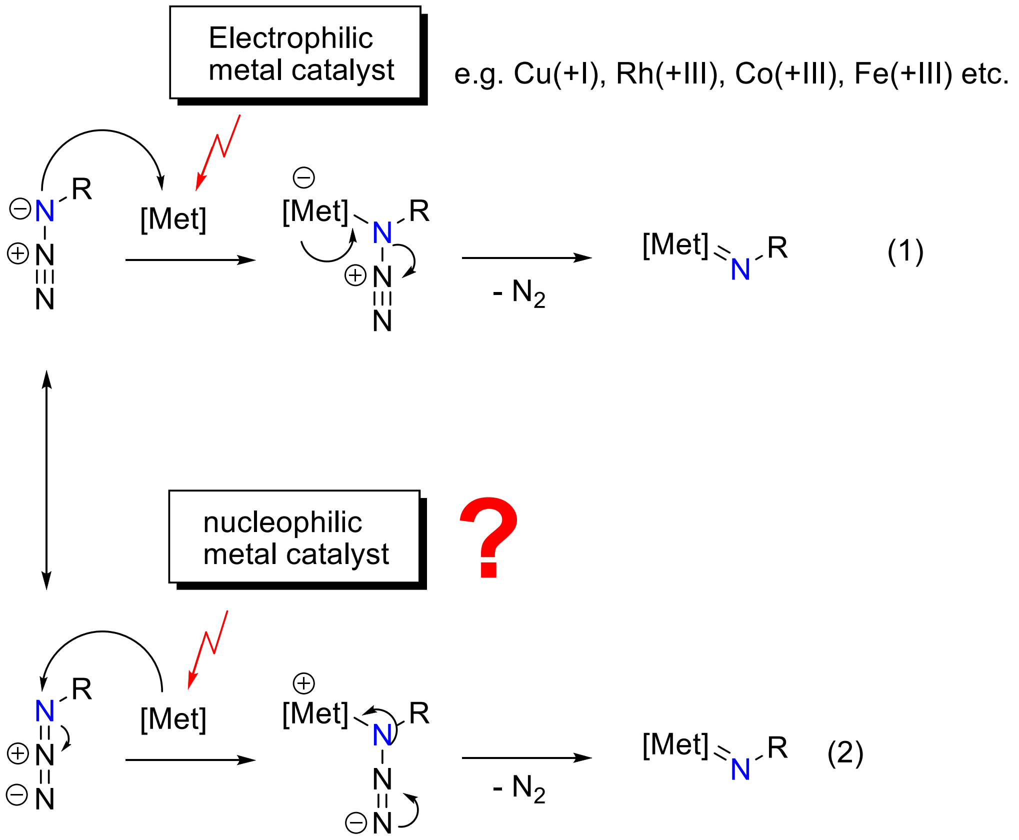
<u>Case 2</u>: Fe-catalyzed carbene transfer reactions



a: 10 Mol-% TBAFe, 1.2 equiv. EDA , 1,2-dichloroethane, 60 °C, 18 h.
b: 10 Mol-% TBAFe, 1.2 equiv. EDA, 1.5 Äquiv. $AsPh_{3,}$ 1,2-dichloroethane, 60 °C, 18 h.
c: 10 Mol-% TBAFe, 1.2 equiv. EDA, 1,2-dichloroethane, 60 °C, 2 h.

ACIE **2012**, *51*, 5351

Case 3: Fe-catalyzed nitrene transfer



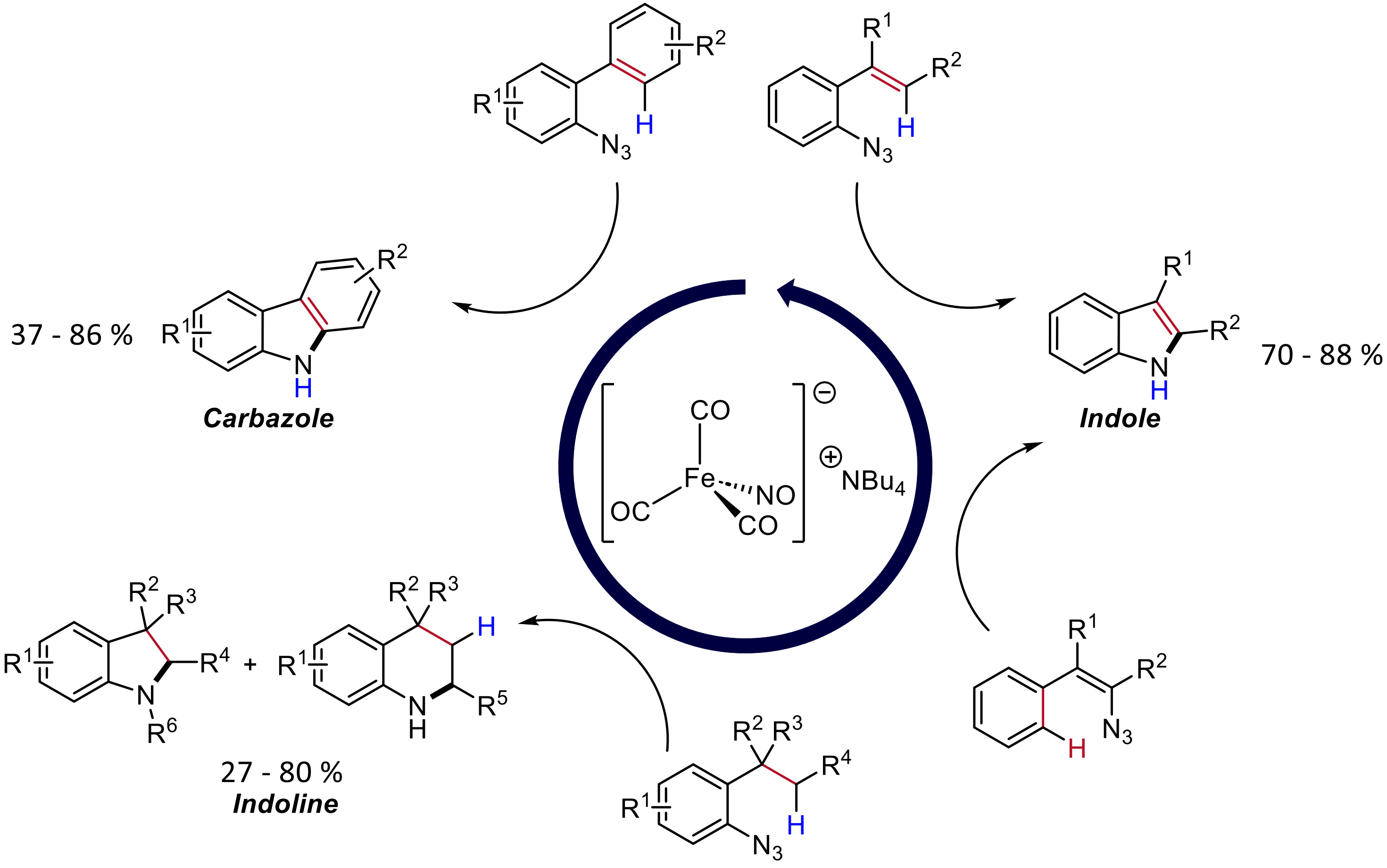
Electrophilic metal catalyst

e.g. Cu(+I), Rh(+III), Co(+III), Fe(+III) etc.

nucleophilic metal catalyst

?

Case 3: Fe-catalyzed C(sp²)-H- and C(sp³)-H-bond amination



ACIE **2017**, *56*, 10582

Fe-complexes with „gold-type“ reactivity? A(n) (alchimistic) vision??

Facts:

- Iron is not gold
- Gold possesses unique catalytic properties
- Relativistic effects are considered (strong binding of 6-s-electrons, weak binding of 5-d-electrons) to be responsible for the alkynophilicity of Au(I)-/Au(III)-complexes

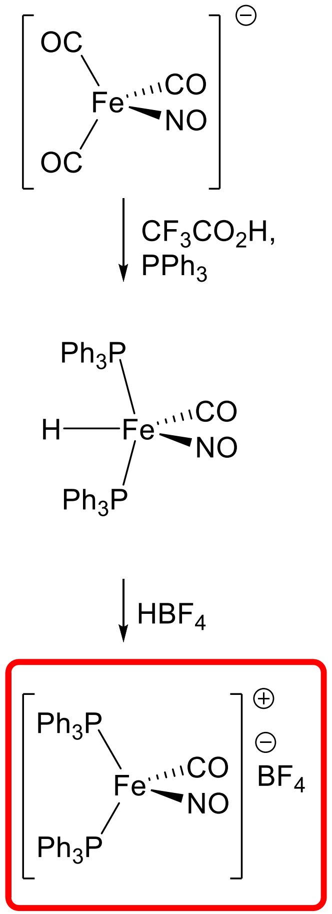
(Review: *Nature* 2007, *446*, 395)

Fiction:

- Ligands can mimic the consequence of relativistic (d-electrons in molecular rather than atom orbitals might be more accessible for catalysis)
- Fe(0) is isoelectronic to Rh(I)/Ir(I), Pd/Pt(II) or Au(III); Fe(-II) is isoelectronic to Au(I)

Are cationic Fe(0)-complexes are alkynophilic??

Expanding the scope – cationic Fe-NO-complexes…

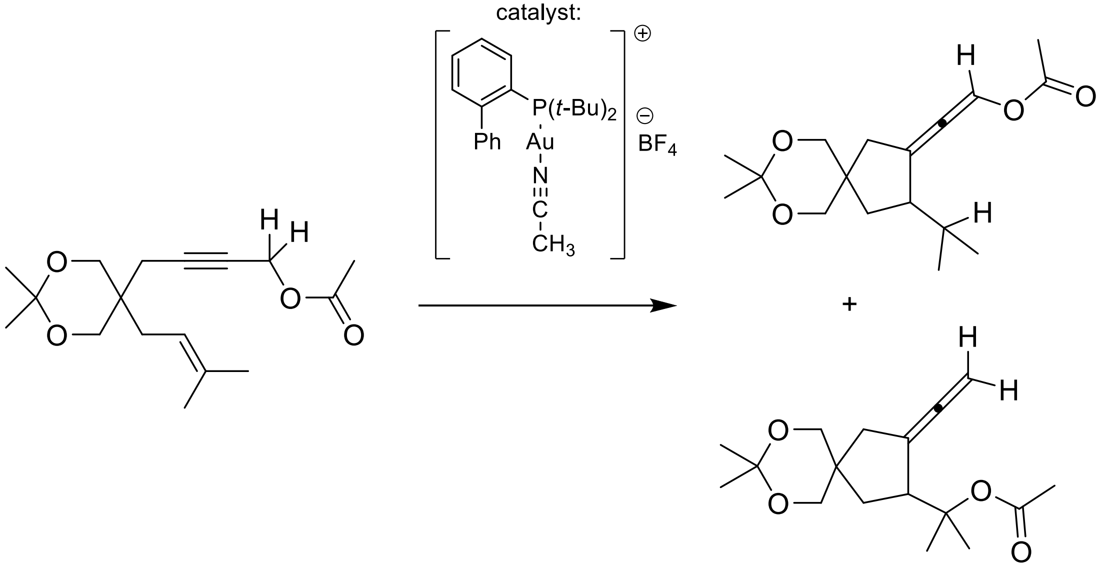


Allylic/benzylic substitutions
Carbene transfer reactions
Nitrene transfer reactions

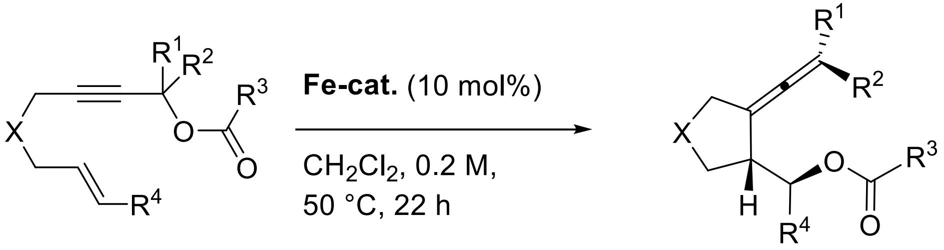
Hydrosilylation
Hydroboration
Borylative cyclisation

Case 4: Au-catalyzed cycloisomerization of enynes

Fensterbank, Malacria (2011):

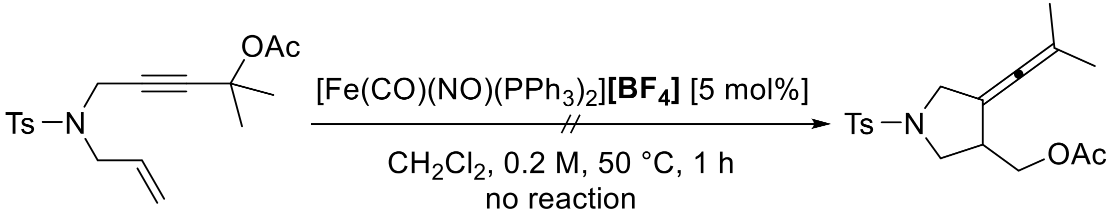


Fe-catalyzed redoxneutral cycloisomerization of enyne acetates



ACS Catalysis **2016**, *6*, 7148

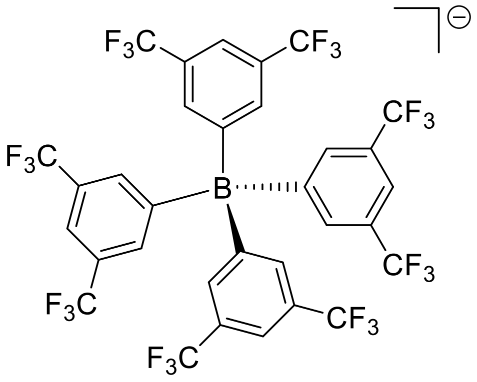
Counter-ion effect



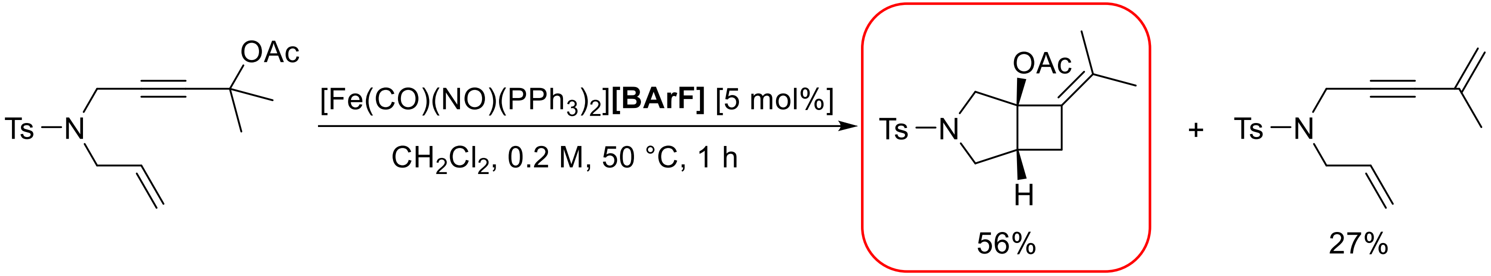
$[Fe(CO)(NO)(PPh_3)_2]$**$[BF_4]$** [5 mol%]

CH_2Cl_2, 0.2 M, 50 °C, 1 h

no reaction



$[BArF]^{\ominus}$



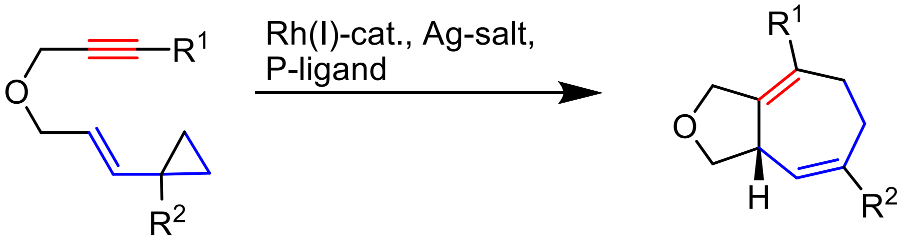
$[Fe(CO)(NO)(PPh_3)_2]$**[BArF]** [5 mol%]

CH_2Cl_2, 0.2 M, 50 °C, 1 h

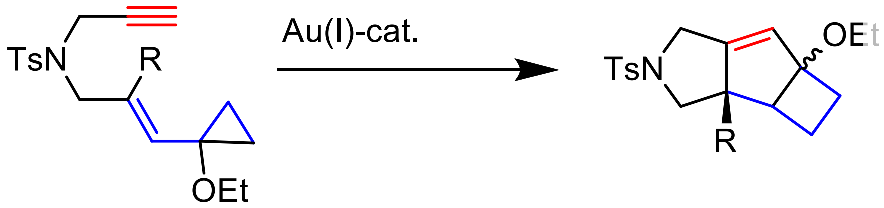
ACIE **2018**, *57*, 13335

Fe-catalyzed cycloisomerization of vinylcyclopropanes

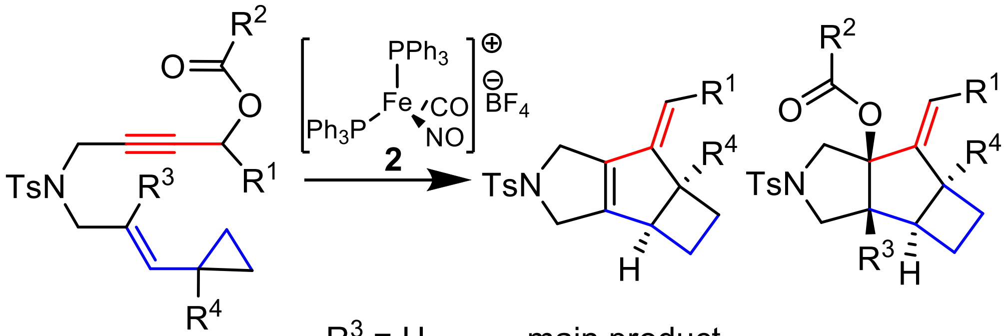
Wender (1995): Rh-catalyzed [5+2]-cycloaddition



Echavarren (2006): Au(I)-catalyzed cycloisomerization



Fe-catalyzed cycloisomerization of vinyl cyclopropanes



$R^3 = H$ main product

$R^3 \neq H$ main product

ACIE **2022**, e202205169

Resumee

- **Catalysis** is an enabling technology for a sustainable future (chemical) process development.
- The majority of process however rely on the use of **precious metal-based catalysts**.
- These metals are not found in the upper earth crust.
- **Earth-abundant metal-catalysis** could offer a solution, but needs to be reinvented

Thank you for your attention!!!!