

Metal Ligand Cooperation in catalyzed dehydrogenations & more mysteries

ETH Zürich

Dr. T. Büttner

Dr. P. Maire

Dr. T. Zweifel

Dr. S. Annen

Dr. R. Rodriguez

Dr. M. Trincado

Dr. D. Banerjee

Dr. T. Gianetti

Dr. H. Schönberg

Dr. F. Krumeich

Dr. J.-V. Naubron

Prof. Dr. M. Reiher

ICCOM-CNR, Firenze

M. Bevilacqua

A. Marchionni

W. Oberhauser

F. Vizza

C. Bianchini

Universiteit van
Amsterdam

Dr. B. de Bruin

Vivek Sinha

*Bertinoro
June 2017*

Financial Support:

ETH Zürich, Swiss National Science Foundation

Energy from renewable resources

Heat of combustion of ethanol: $-1'278.4 \text{ kJ mol}^{-1}$

1 kg EtOH = 28 MJ = 7.7 kWh

The «2'000 W society» (17'500 kWh/year) would need:

2'270 kg EtOH (2900 L) per person per year.

This corresponds to 26 tons of sugar cane.

Under very good conditions, 4'500 m² of land are needed to harvest this amount; «energy density» $\approx 3 \text{ kWh m}^{-2}$.



Presently commercially available solar cells deliver 680 (crystalline) to 320 (amorphous) kWh m⁻²

Reaction

Review: Trincado, Banerjee, Grützmacher, Energy & Environ. Sci. 2014, 7, 2464–2503.

 ΔH_R
(kJ mol⁻¹)H₂
(wt%) ΔE_F
(kJ mol⁻¹)

89.1

6.2

-152.9



5.5

6.6

-236.6



-20.9

4.2

-262.9



-14.9

4.3

-256.9



53.3

12.0

-672.7



54.3

6.2

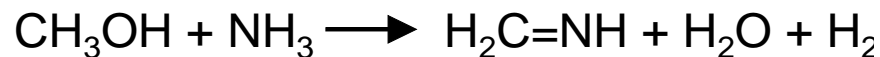
-429.5



64.9

8.1

-419.1



120

4.1

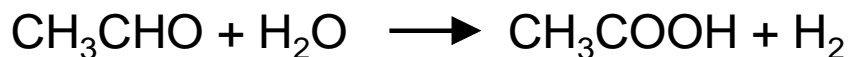
-122.0



63.3

4.3

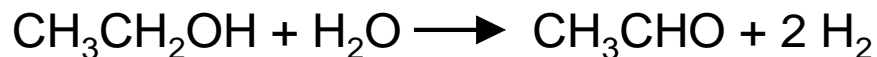
-178.7



-20.5

3.2

-262.5



42.8

6.2

-442.4



172.4

12.0

-1280.0



22.6

4.3

-461.4



41.6

6.3

-442.4



37.5

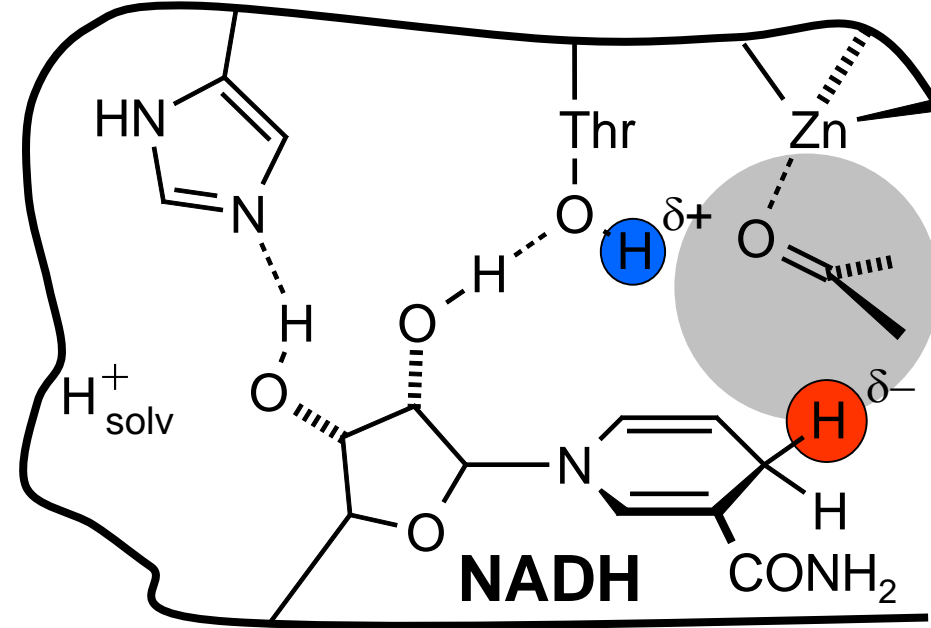
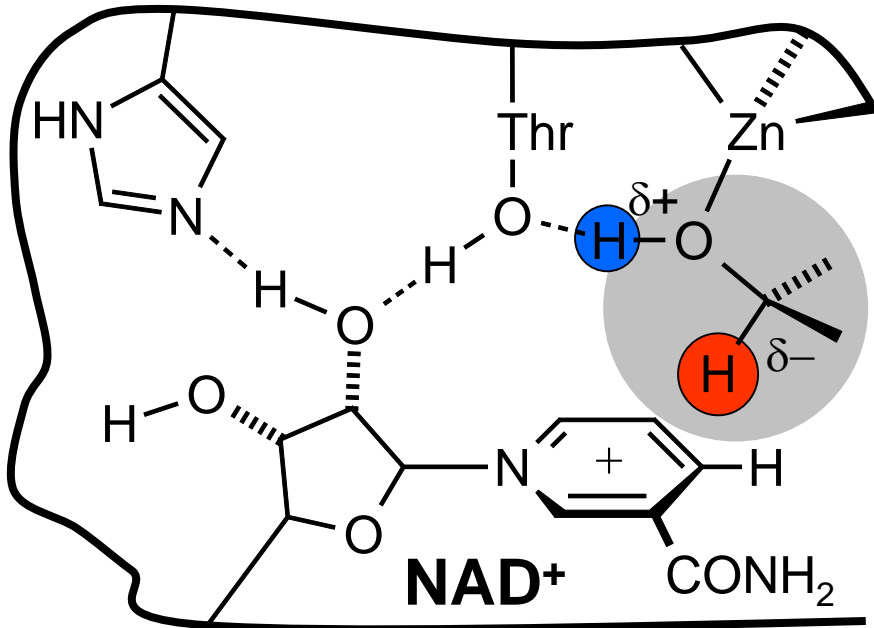
3.3

-204.5

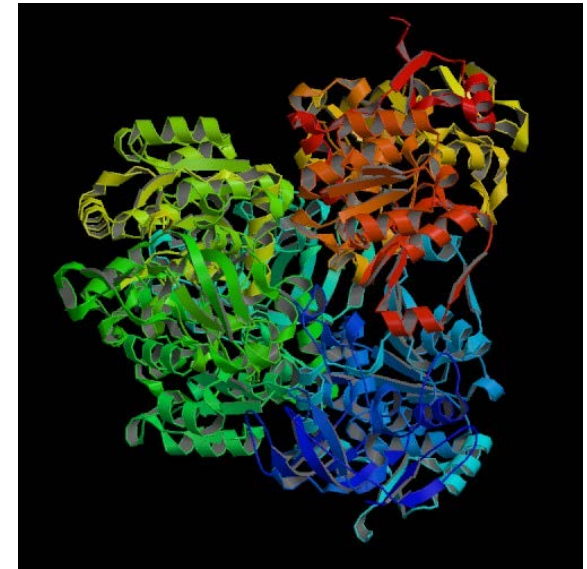
$$\Delta E_F = \Delta H_R(n \text{H}_2 + n/2 \text{O}_2) - \Delta H_R$$

$$\Delta H_R(\text{H}_2 + 0.5 \text{O}_2) = -242 \text{ kJ mol}^{-1}$$

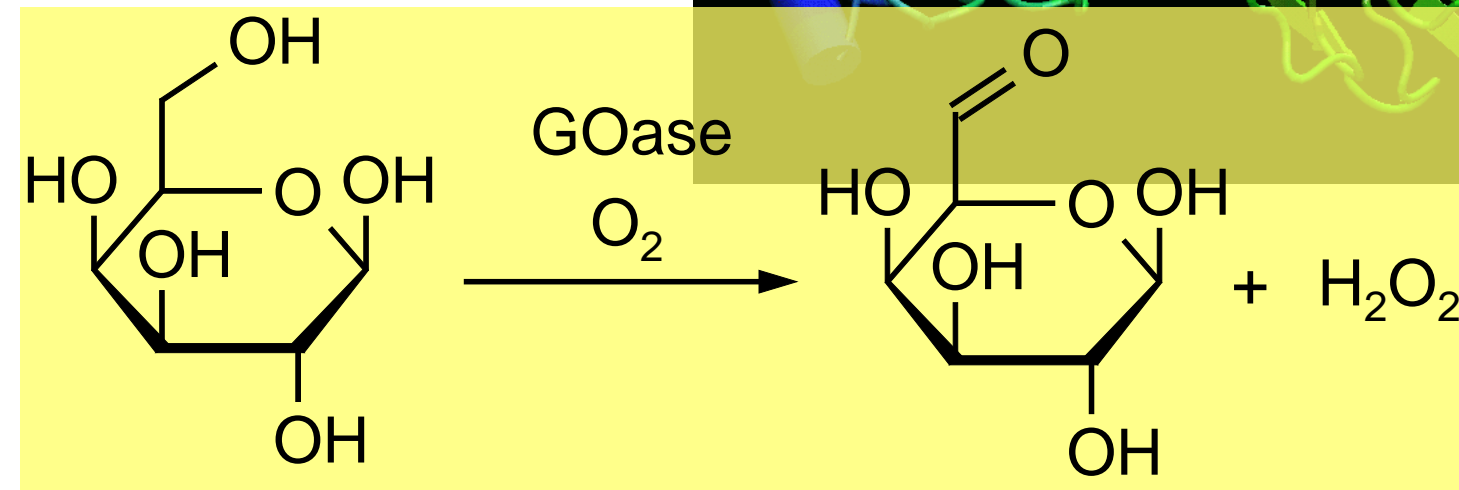
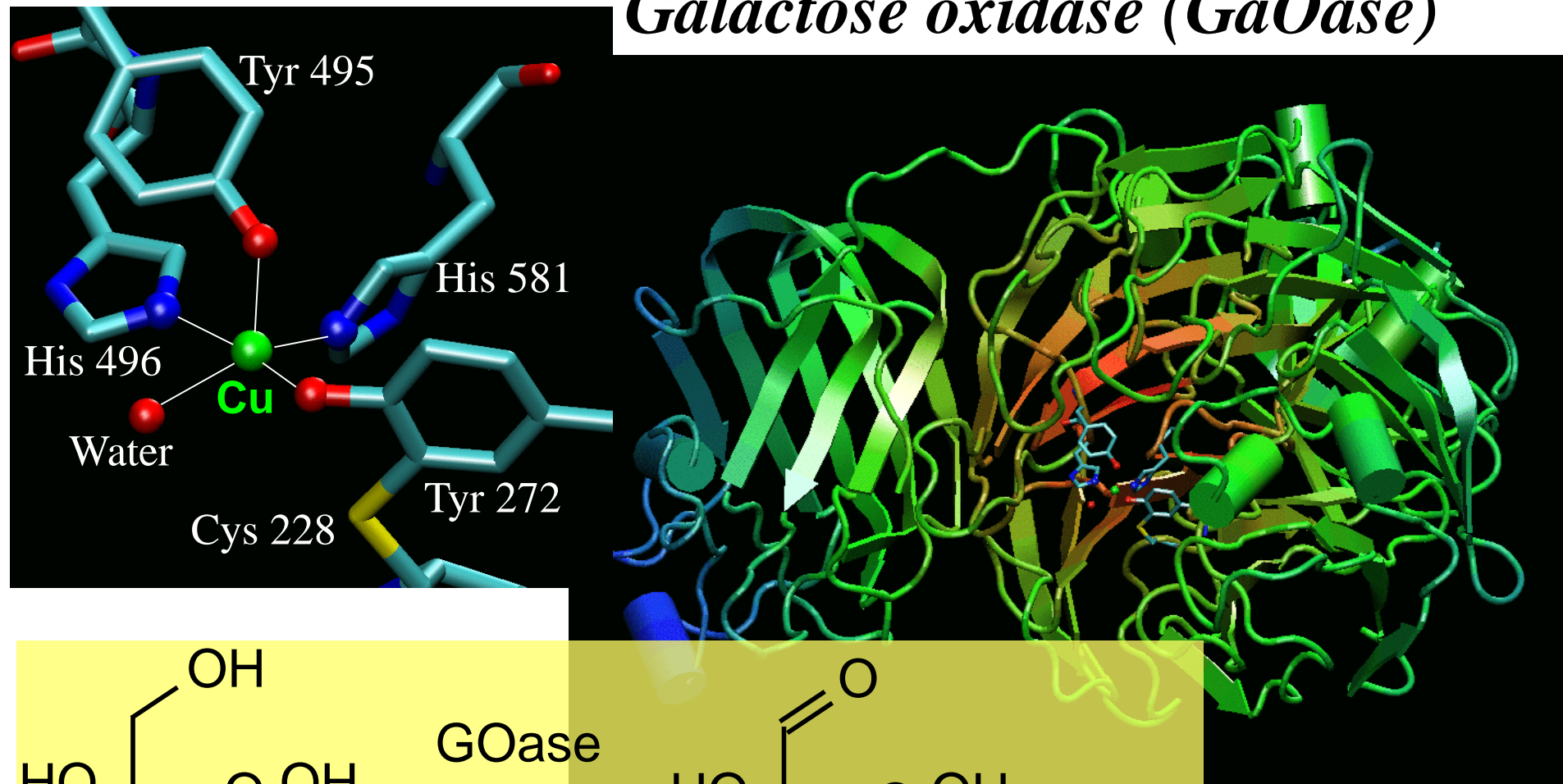
How does Mother Nature convert alcohols: Alcohol dehydrogenase (ADH)



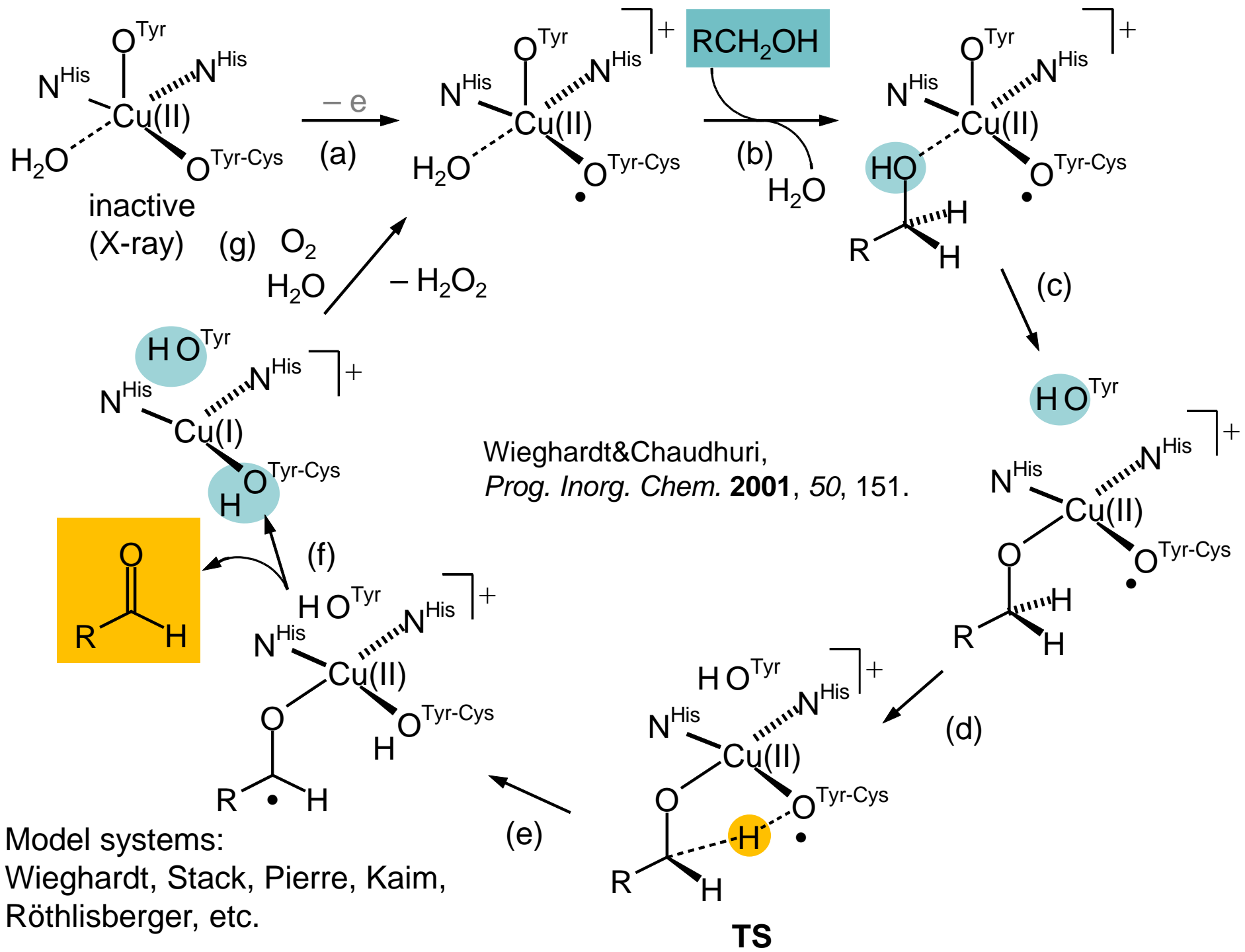
- Ribose and nicotinamide parts involved
- Positioning of the cofactor is critical
- quantum tunneling involved in hydride equivalent transfer



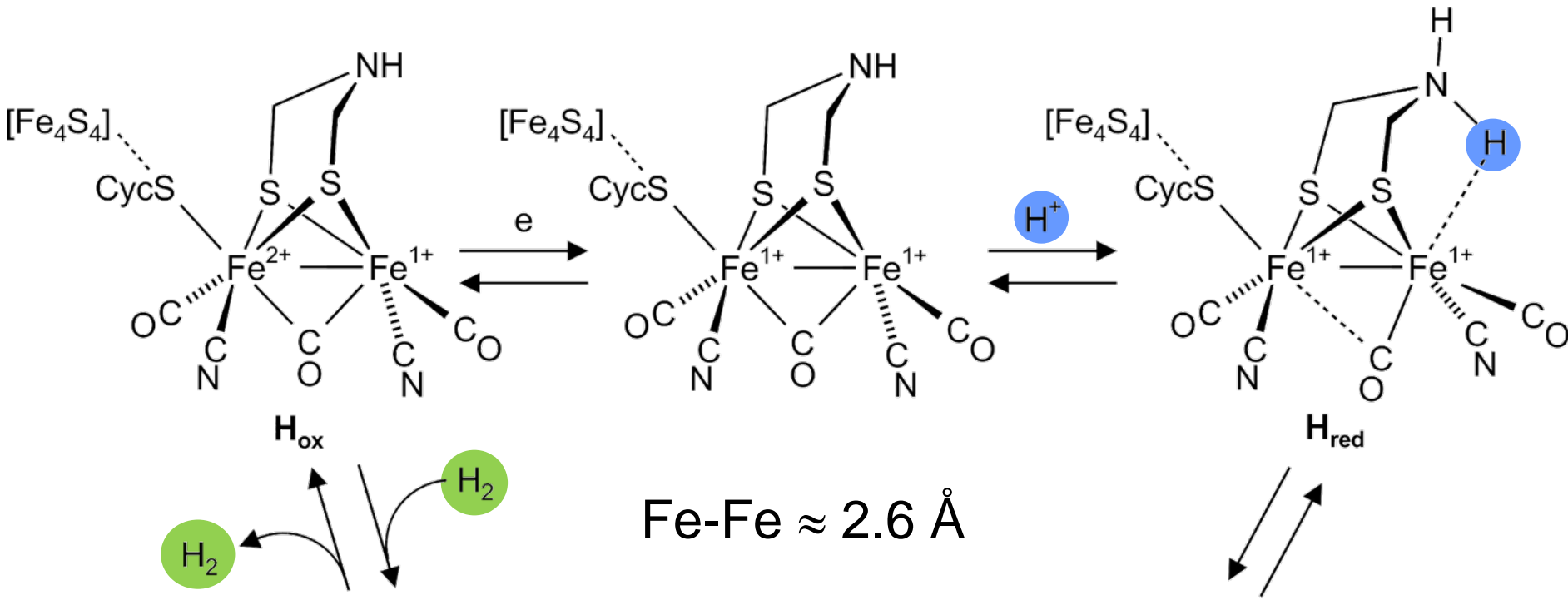
Galactose oxidase (GaOase)



for EtOH \rightarrow MeCH=O:
 $\Delta H_r \approx -25 \text{ kcal mol}^{-1}$

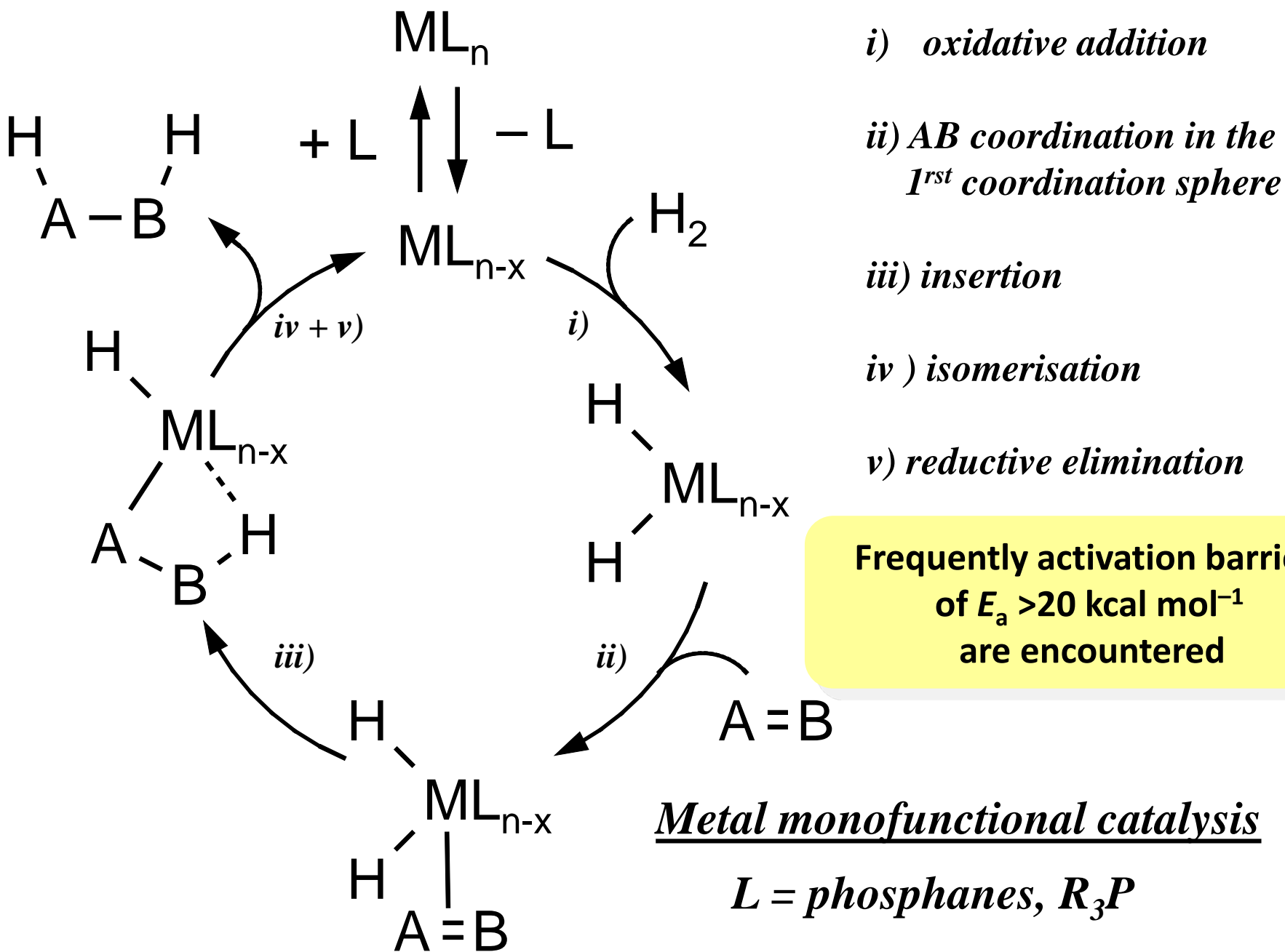


Cooperative Ligands in Biological Systems: [Fe,Fe] Hydrogenase



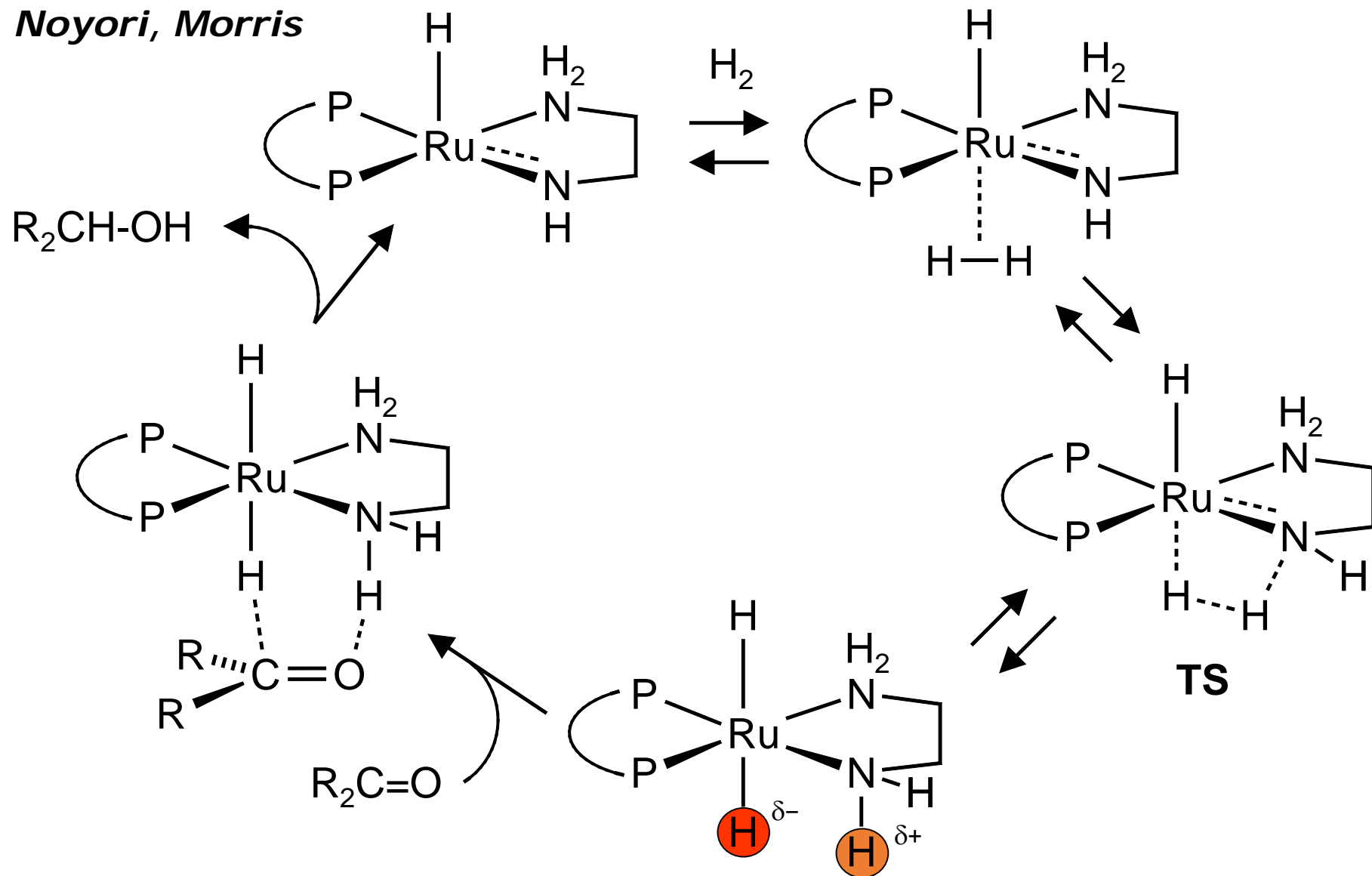
***A “cooperating ligand”
in a transition metal complex
participates directly
in a bond activation reaction and undergoes
a reversible chemical transformation.
The metal and the ligand cooperate in
a synergistic manner and their interplay
facilitates a chemical process.***

„Classical“ man-made organometallic catalytic cycle for hydrogenation

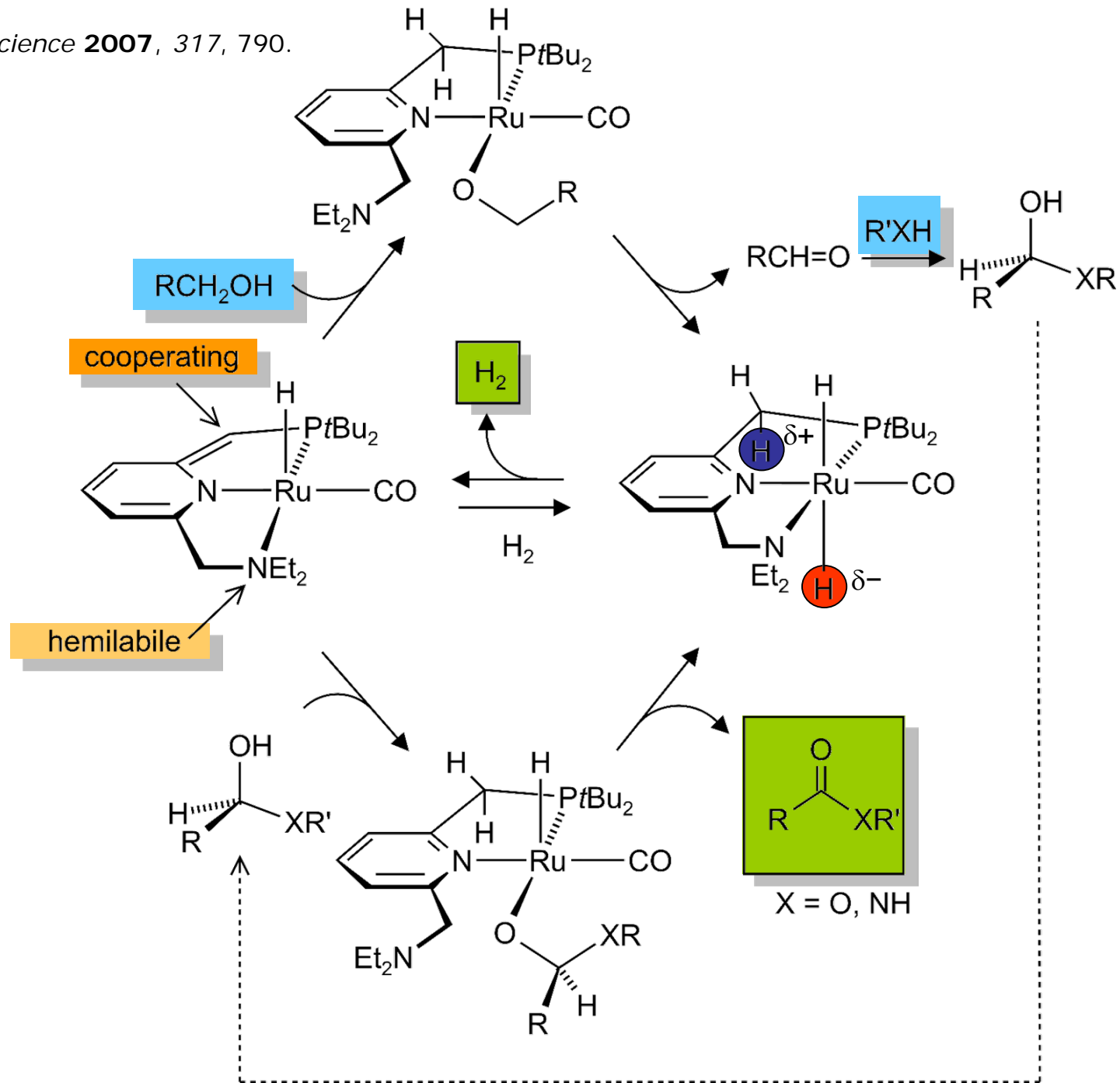


Examples (1): Metall Amido Complexes

Noyori, Morris



Milstein et al., *Science* **2007**, 317, 790.

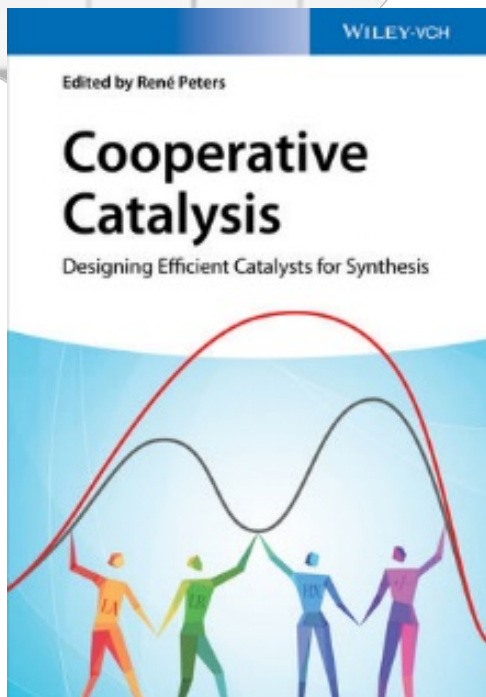


Keywords:
cooperating ligands -
homogeneous catalysis -
metal complexes



Angewandte
International Edition
Chemie

12235 www.angewandte.org



M. Trincado, H. Grützmacher
DOI: 10.1002/9783527681020.ch3

V. Lyaskovskyy, B. de Bruin
Redox Non-Innocent Ligands: Versatile New Tools to Control Catalytic Reactions, *ACS Catal.* **2012**, 2, 270–279.

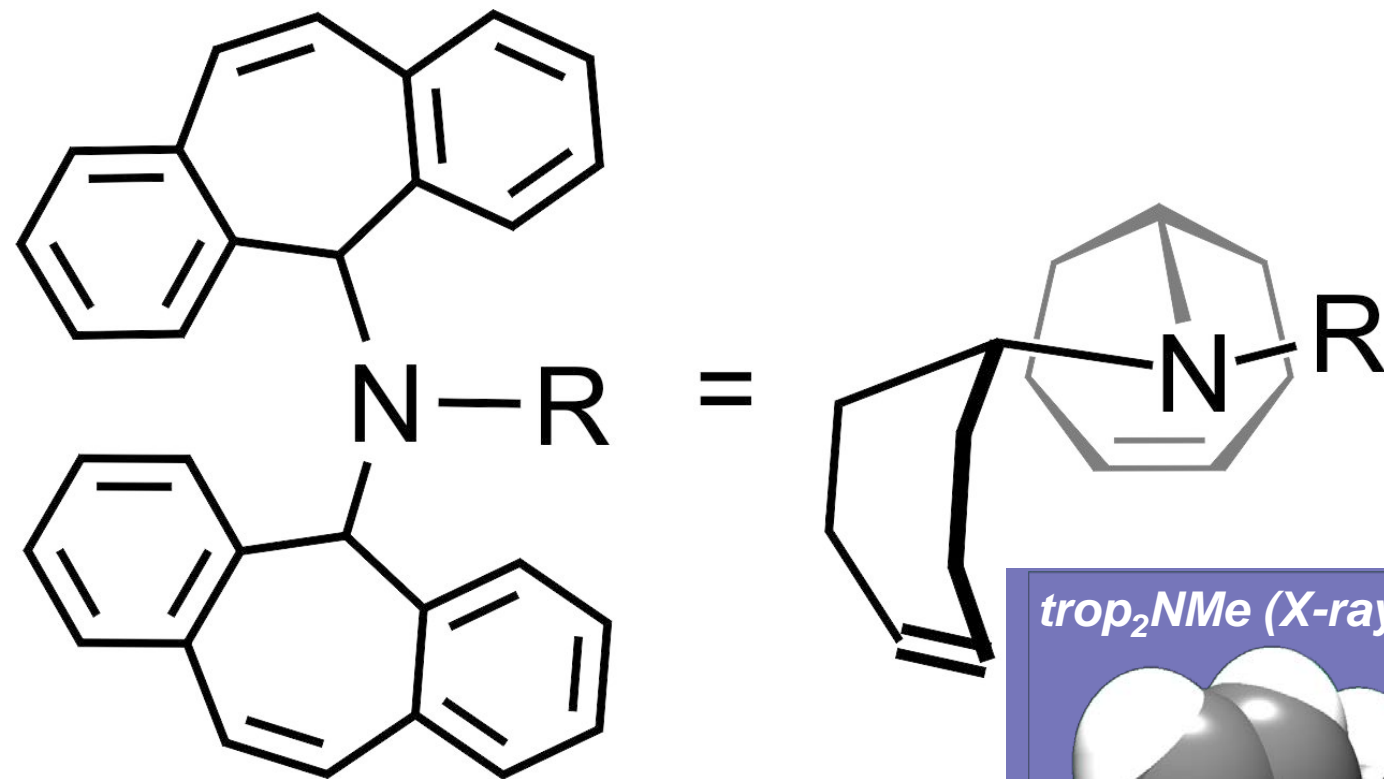
V. T. Annibale, D. Song, *Multidentate actor ligands as versatile platforms for small molecule activation and catalysis*, *RSC Adv.*, **2013**, 3, 11432–11449.

M. Devillard, G. Bouhadir, D. Bourissou, *Cooperation between Transition Metals and Lewis Acids: A Way To Activate H₂ and H-E bonds*, *Angew. Chem. Int. Ed.* **2015**, 54, 730 – 732.

J. R. Khusnutdinova, D. Milstein, *Metal–Ligand Cooperation*, *Angew. Chem. Int. Ed.* **2015**, 54, 12236 – 12273.

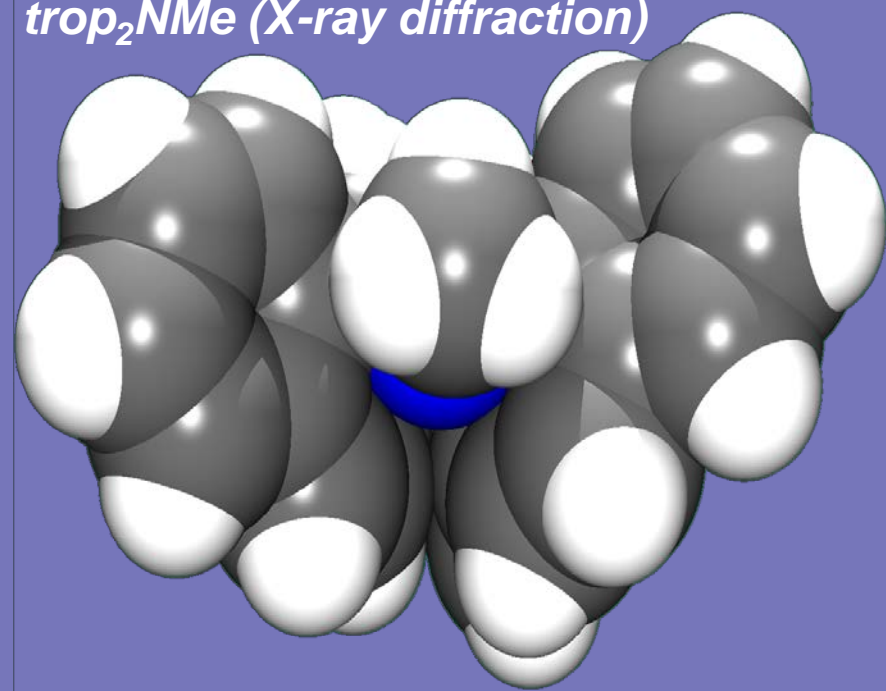
D. G. A. Verhoeven, M.-E. Moret, *Metal–ligand cooperation at tethered π -ligands*, *Dalton Trans.*, **2016**, 45, 15762–15778.

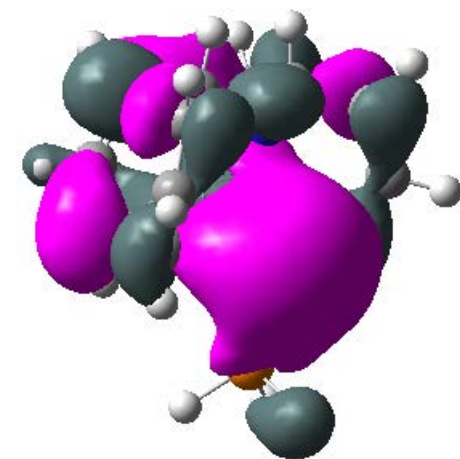
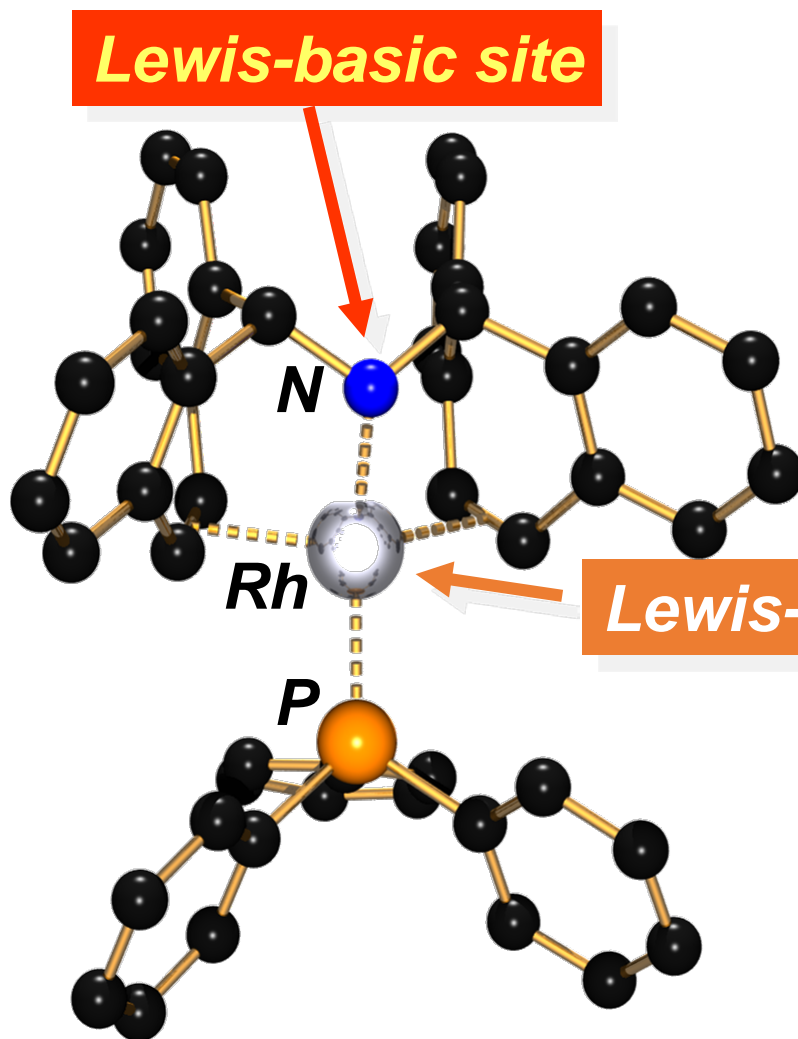
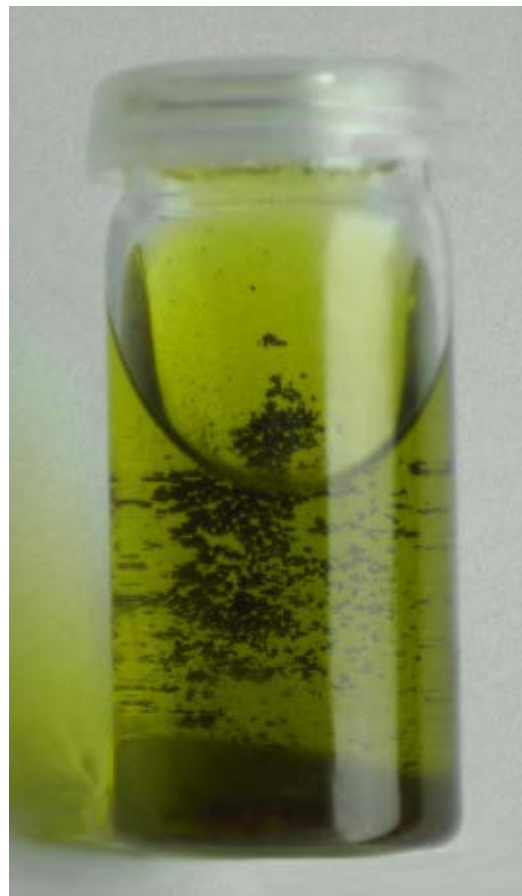
Tropamine: A concave shaped rigid bis(olefin)amine ligand



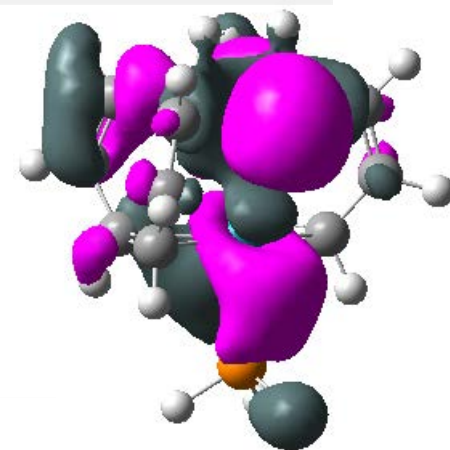
$\text{R} = \text{H}$, alkyl, aryl, etc.

trop₂NMe (X-ray diffraction)





LUMO

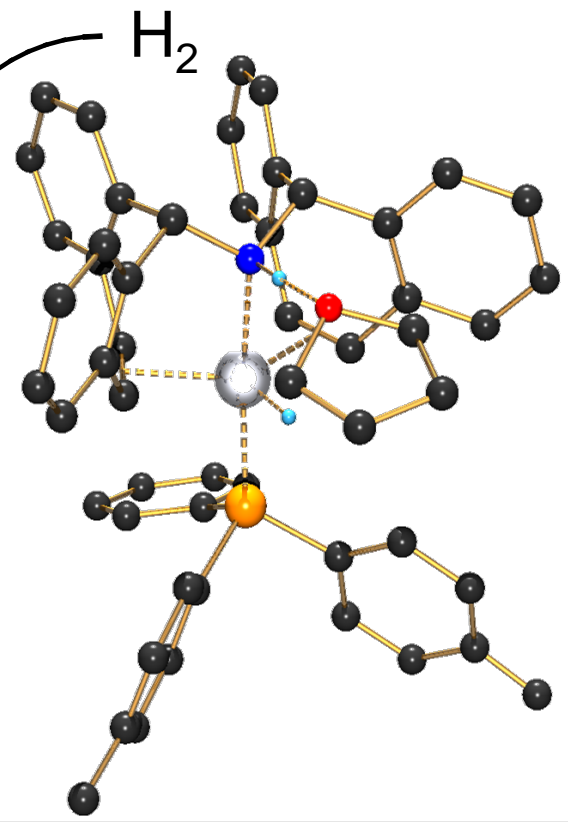
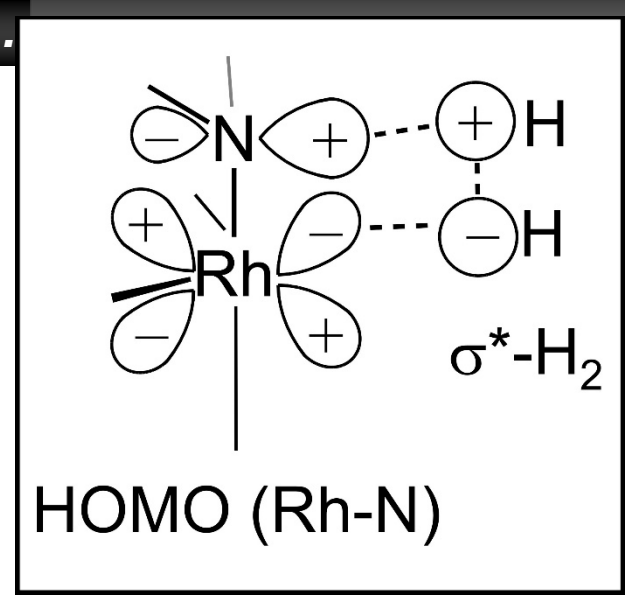
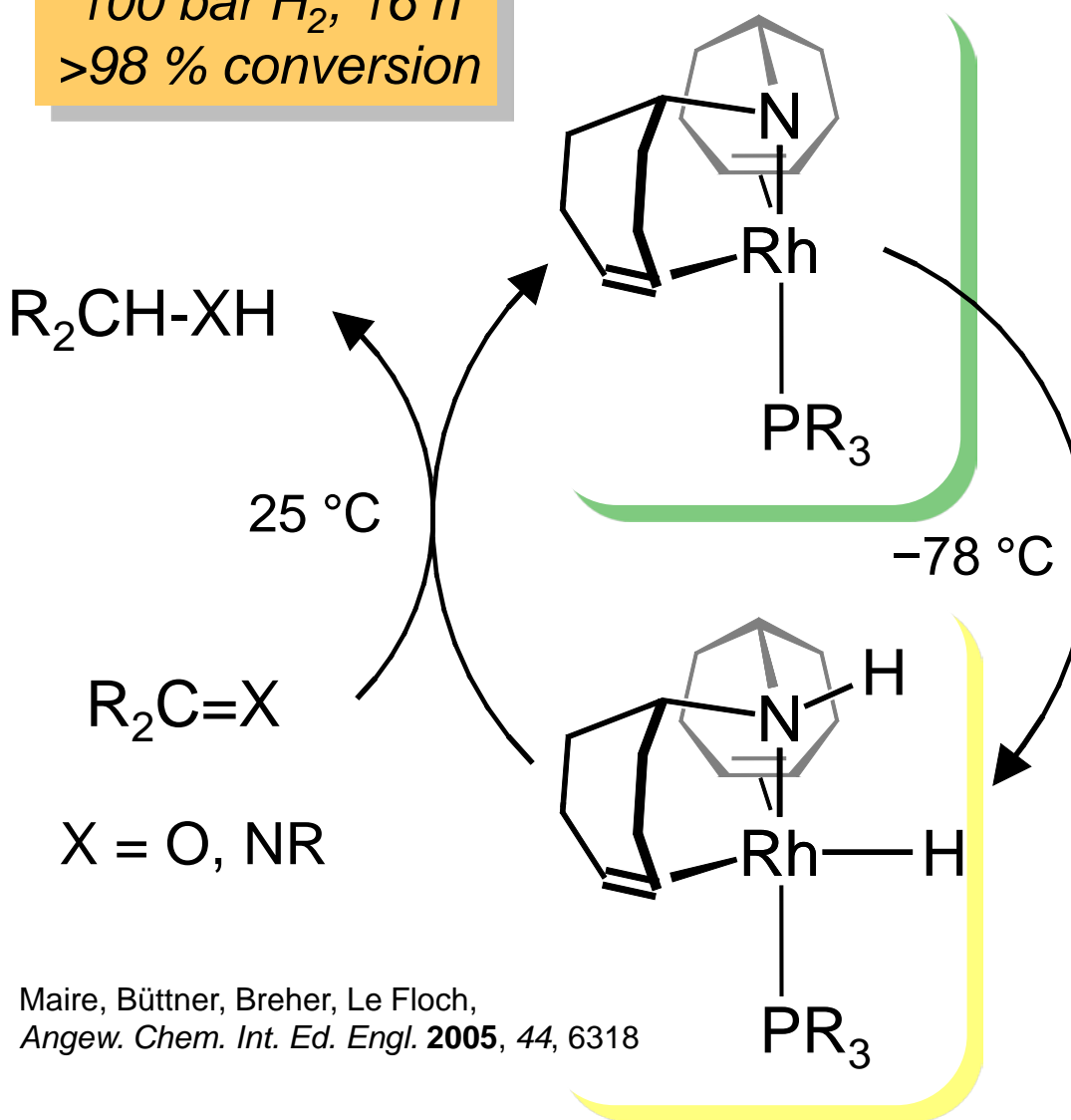


HOMO

Heterolytic H₂ cleavage and catalytic hydrogenation....

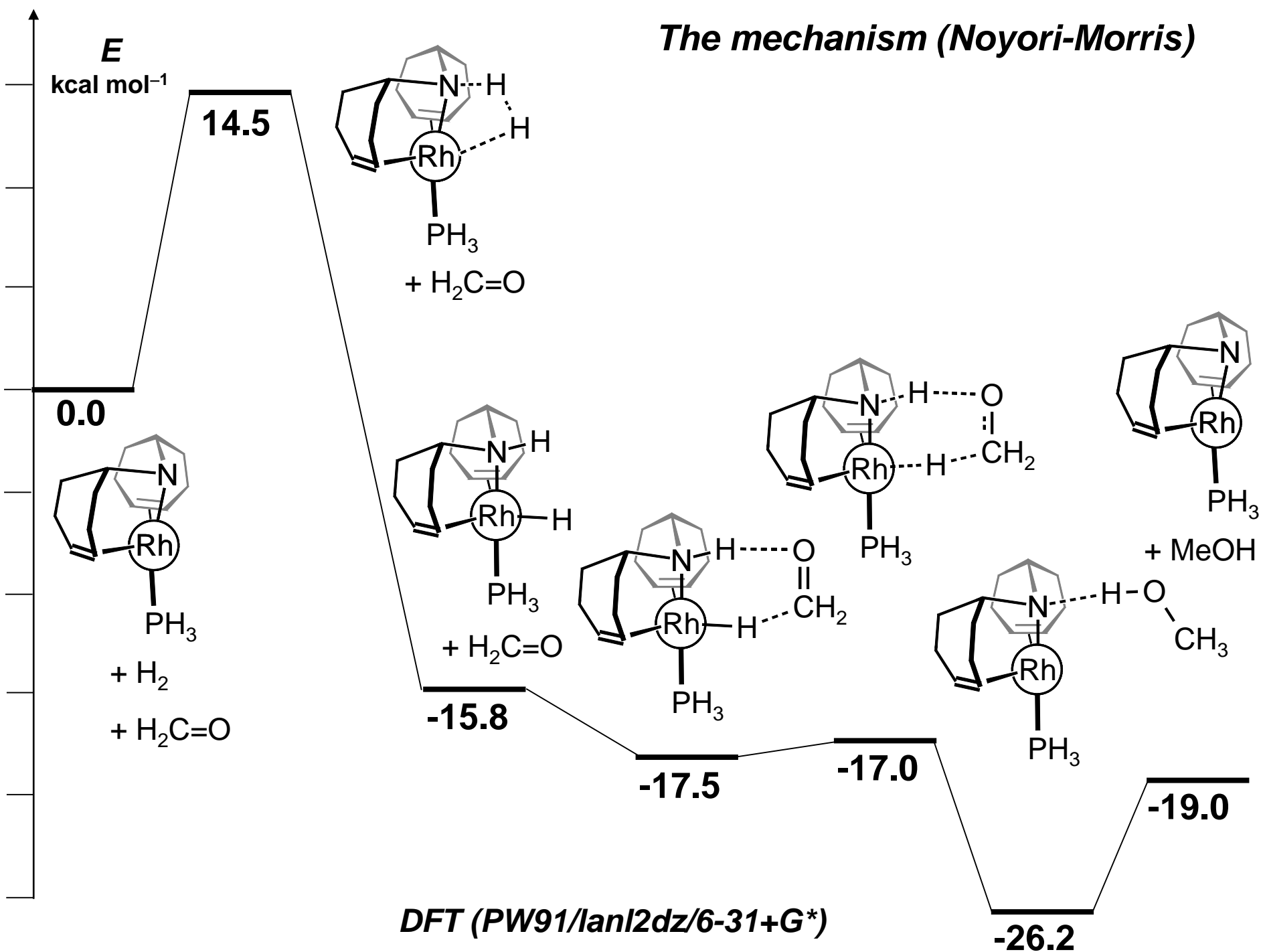
CATALYSIS

< 0.1 mol% cat
100 bar H₂, 16 h
>98 % conversion

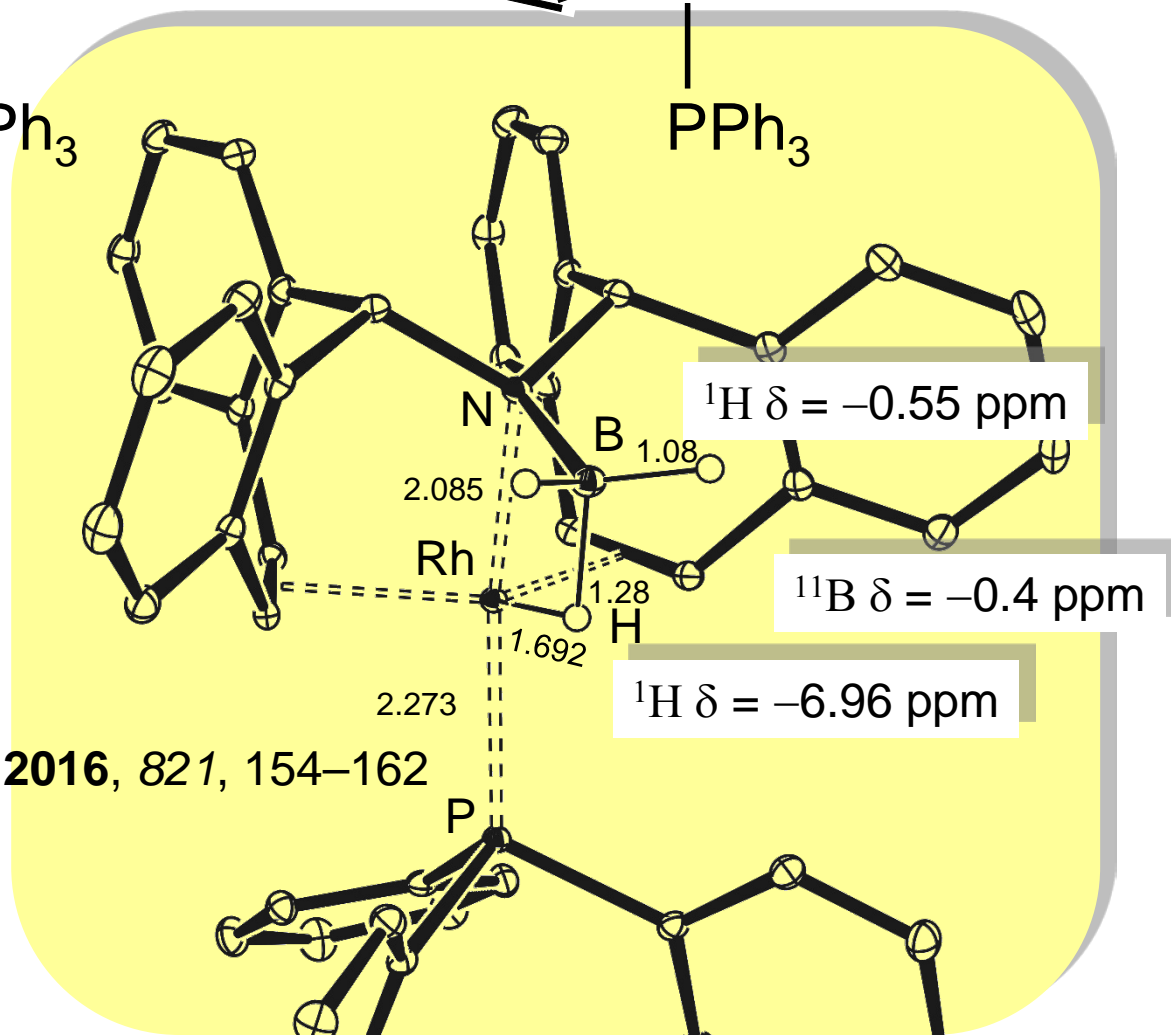
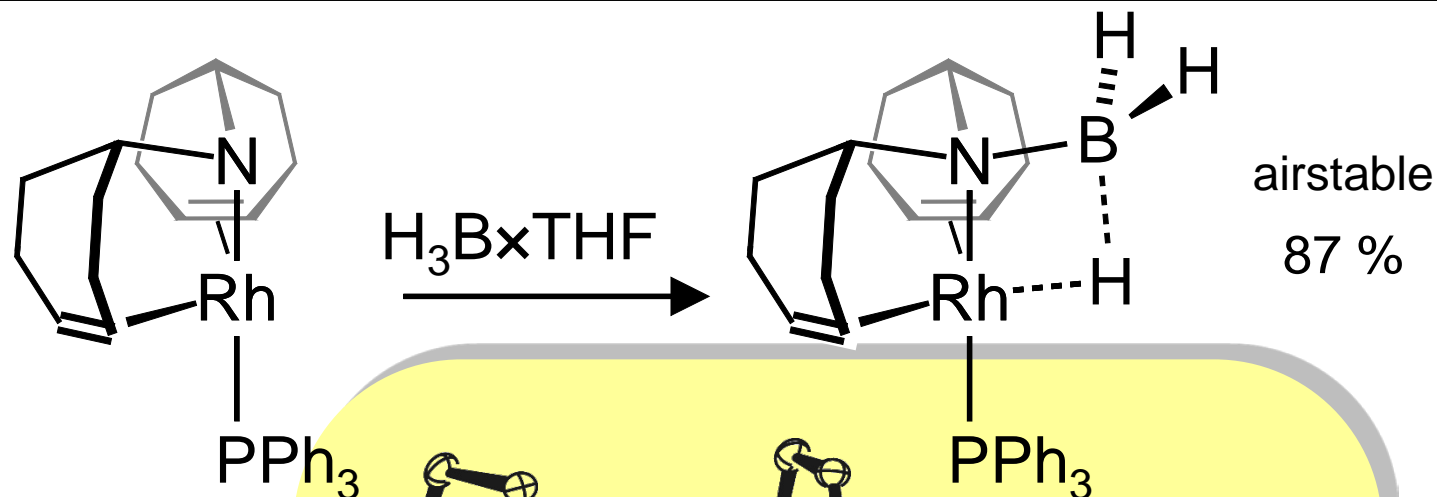


Maire, Büttner, Breher, Le Floch,
Angew. Chem. Int. Ed. Engl. **2005**, 44, 6318

The mechanism (Noyori-Morris)



Addition of BH_3 across a Rh-N bond



F. Müller et al.,
J. Organomet. Chem. **2016**, 821, 154–162

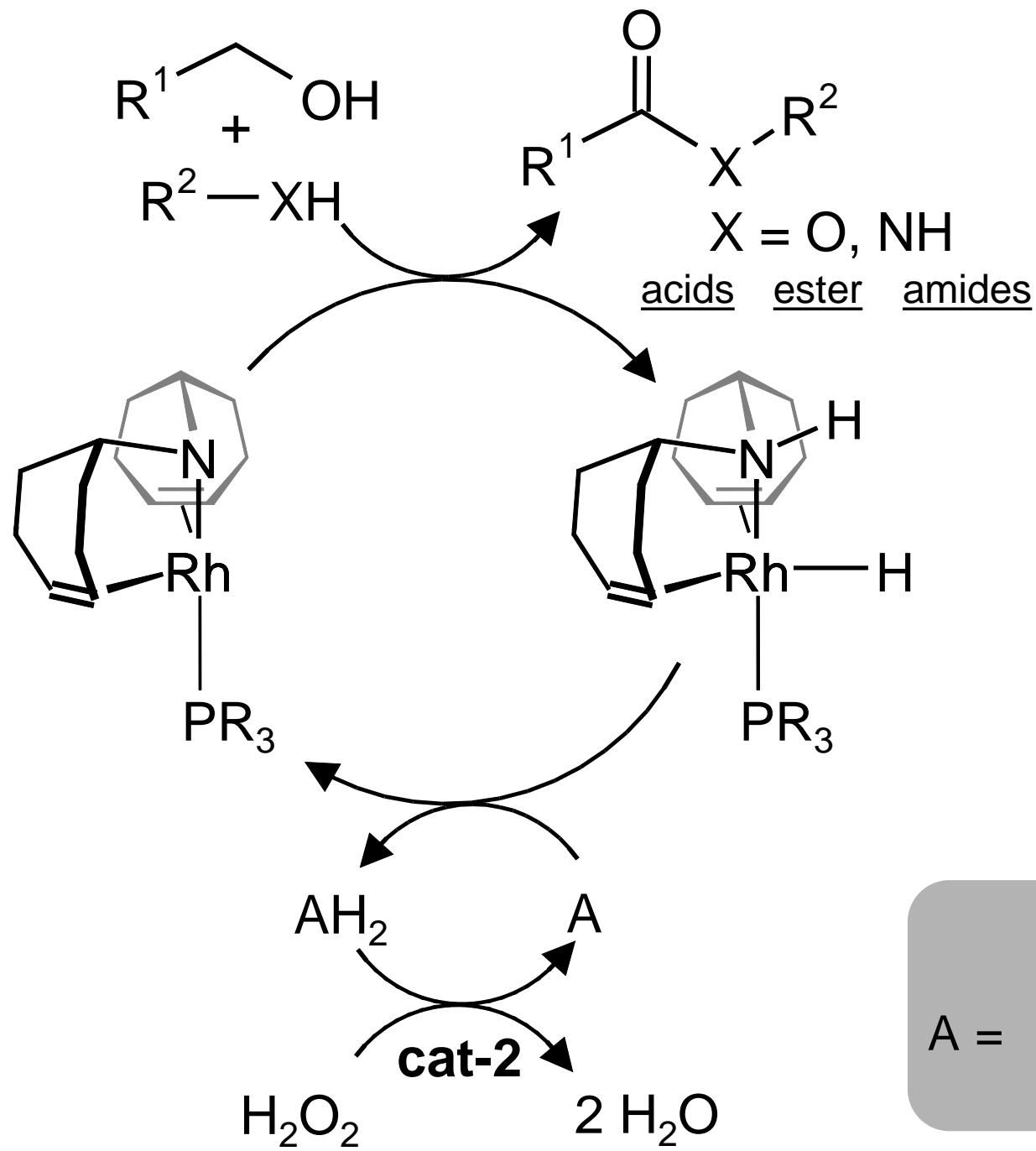


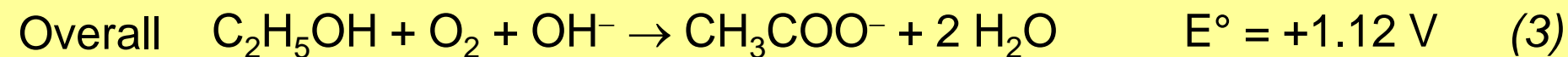
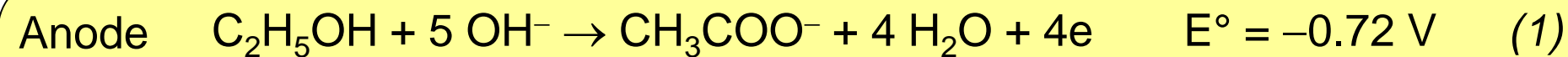
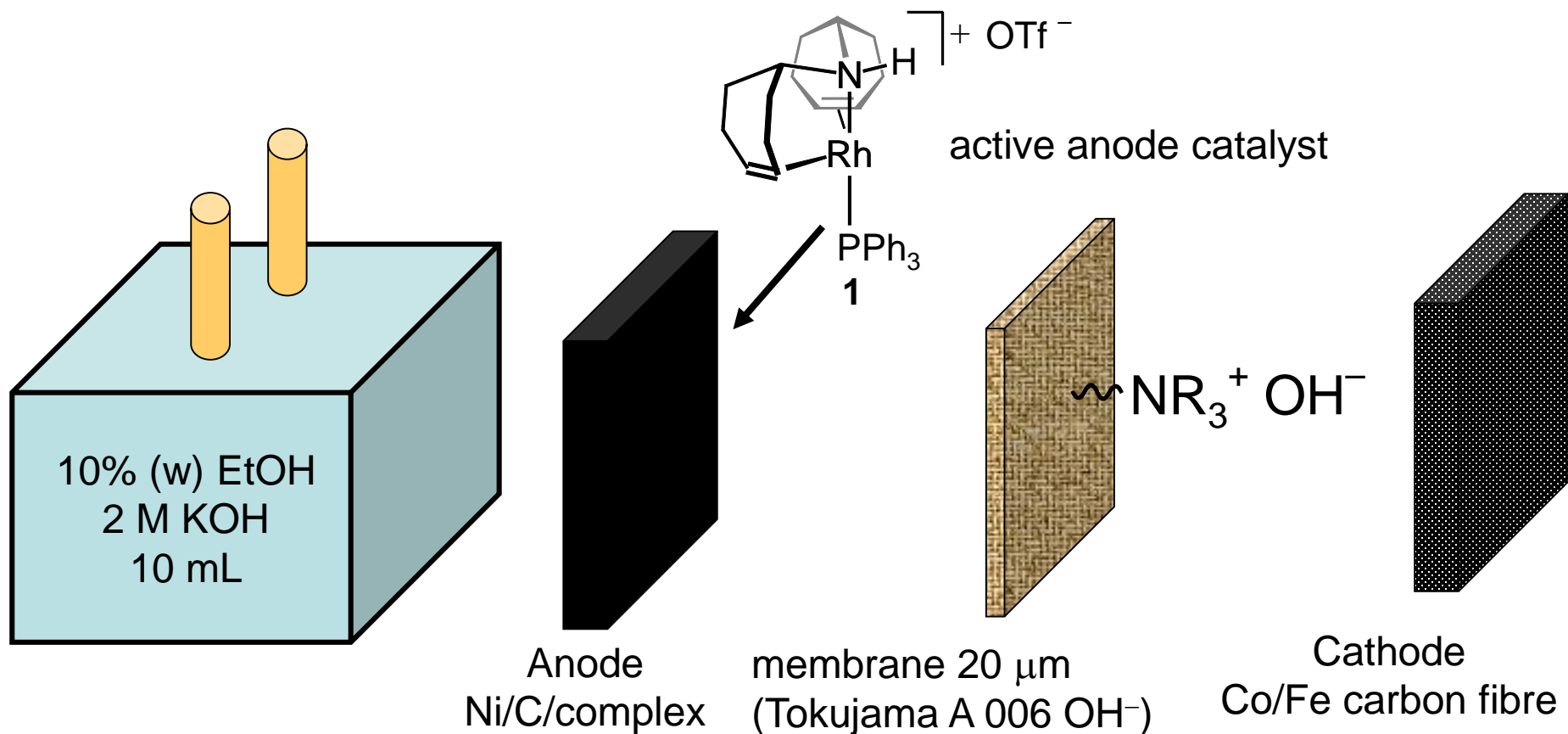
Table 1 Scope of rhodium-catalyzed DHC of polyols to carboxylic acids^a

entry	Alcohol	Product	rt	Yield (%) ^b
1	2a	3a	2h	99
2	2b	3b	2h	98
3	2c	3c	5h	91 (85) ^c
4	2d	3c(rac)	18h	89 ^d
5	2e	3d	8h	98
6	2f	3d	10h	95 ^d
7	2g	3e	12h	97
8	2h	3f	12h	79
9	2i	3g	12h	66 ^e

Table 2 Scope of rhodium-catalyzed DHC of polyols to amides^a

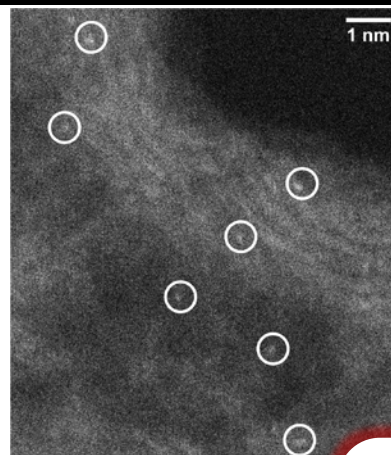
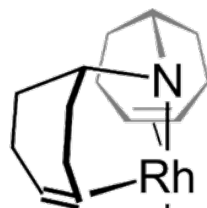
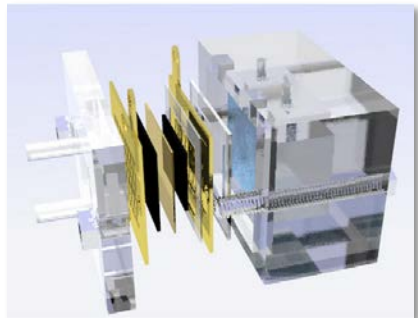
entry	Alcohol	Product	rt	Yield (%) ^b
1	2b	4a	1h	95
2	2c(rac)	4b	1h	90
3	2e	4c	2h	60 ^c (83) ^d
4	2h	4d	8h	90 ^e
5	2j	4e	12h	92 ^f
6	2k	4f	12h	96 ^f
7	2l	4g	12h	37 ^f

Organometallic Fuel Cell (OMFC)

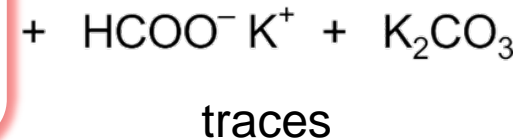
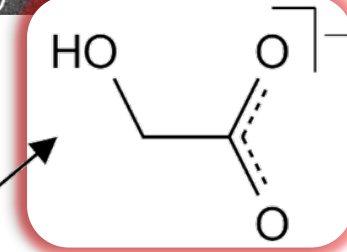
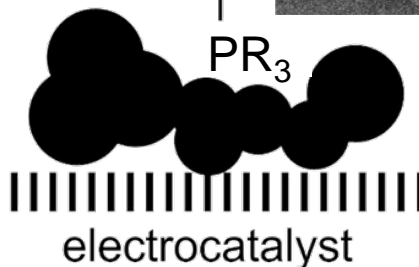
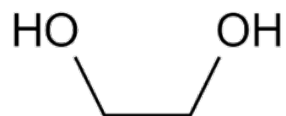
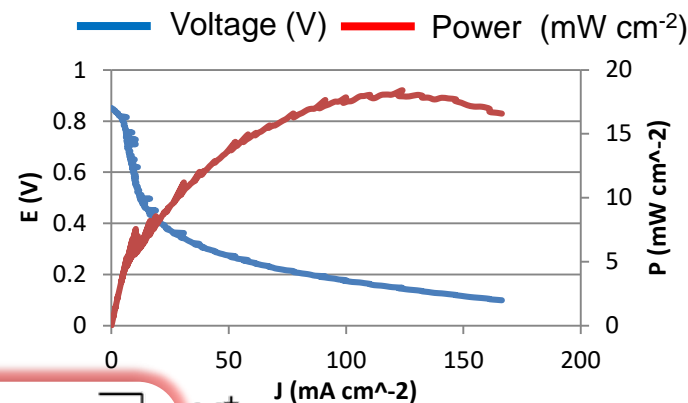


Organometallic Fuel Cell (OMFC): Selective oxidation in active cells

HAADF-STEM (Z contrast) image showing the presence of single atoms of Rh as bright spots

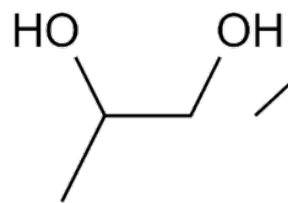


Power Density and Polarization Curves at 80°C

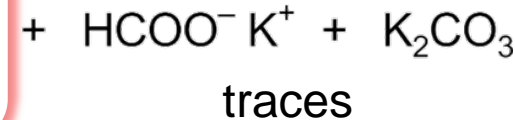
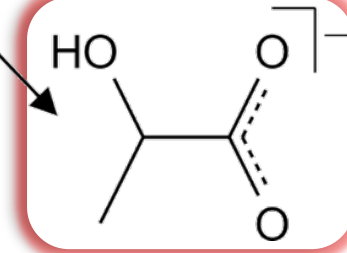


95% glycolate

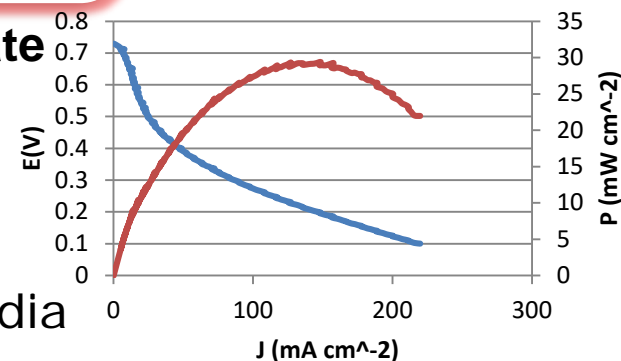
+ ENERGY



Ketjenblack
80°C
5wt% alcohol
2 M KOH(aq)

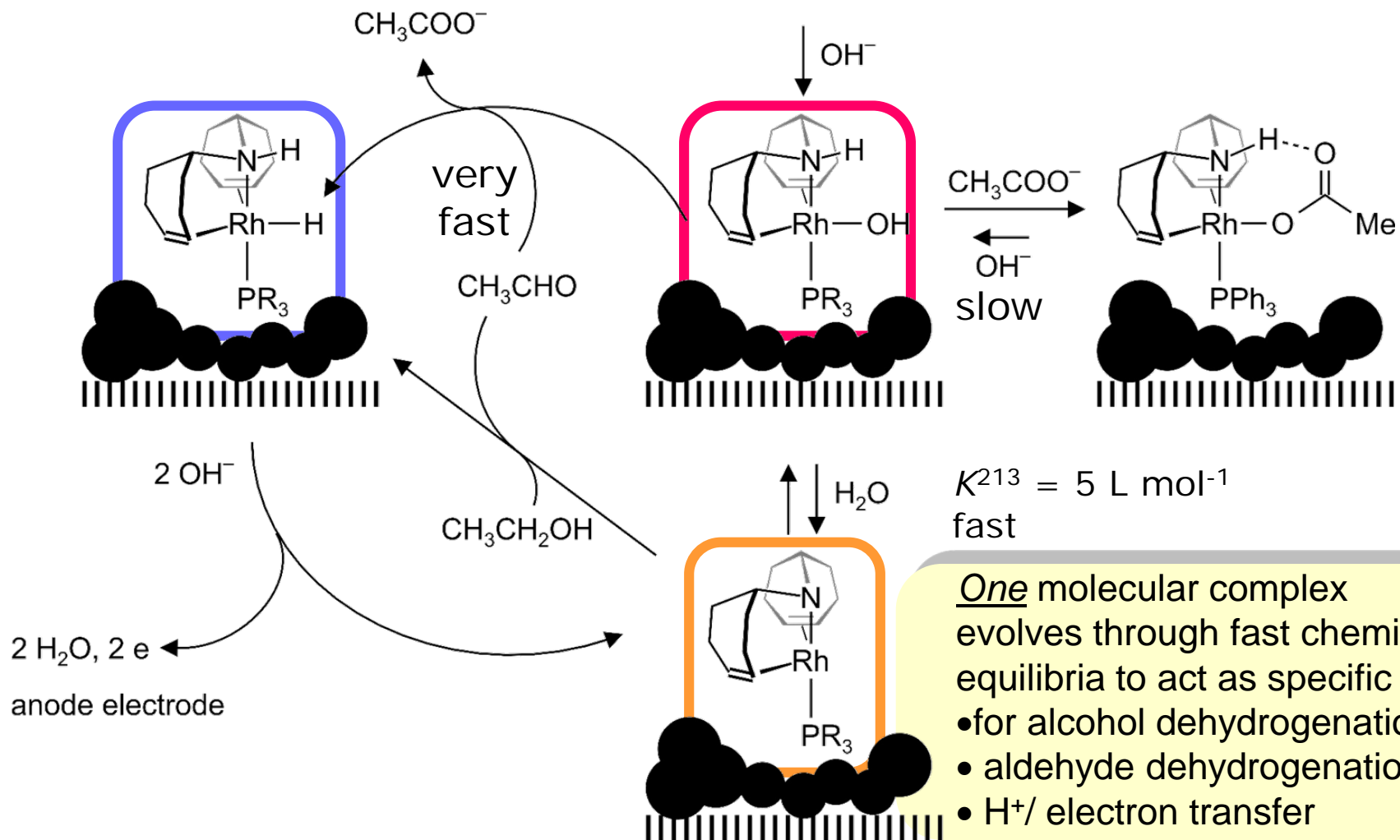
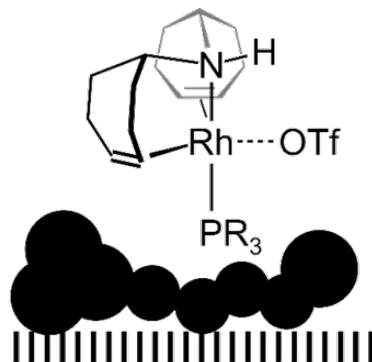
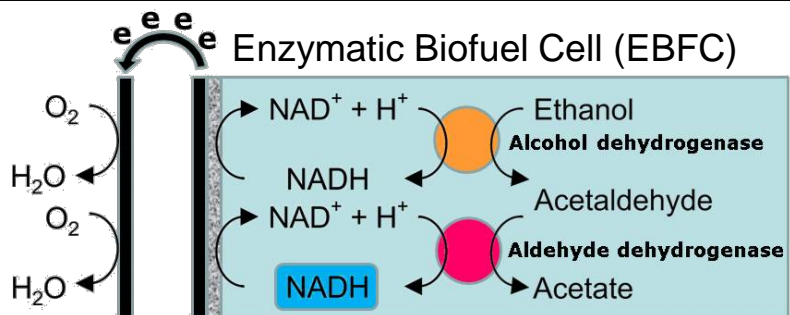


90% lactate



> 50% conversion

the highest specific activities (> 18 mA/μg Rh) and **selectivity** for alcohol oxidation in alkaline media



One molecular complex evolves through fast chemical equilibria to act as specific catalyst

- for alcohol dehydrogenation
- aldehyde dehydrogenation
- H^+ / electron transfer

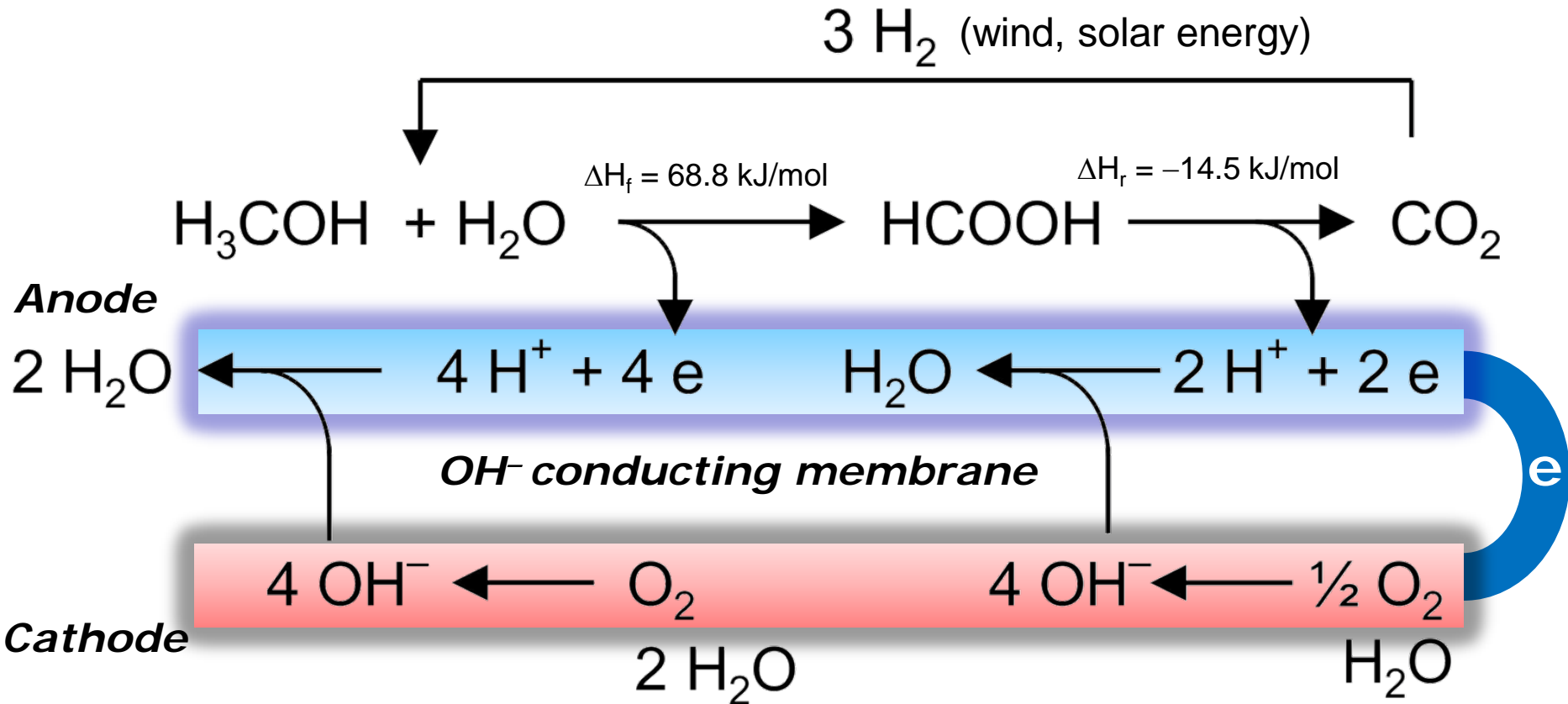
Methanol as fuel

G.A. Olah, A. Goeppert, G.K. Surya Prakash, *The Methanol Economy*.

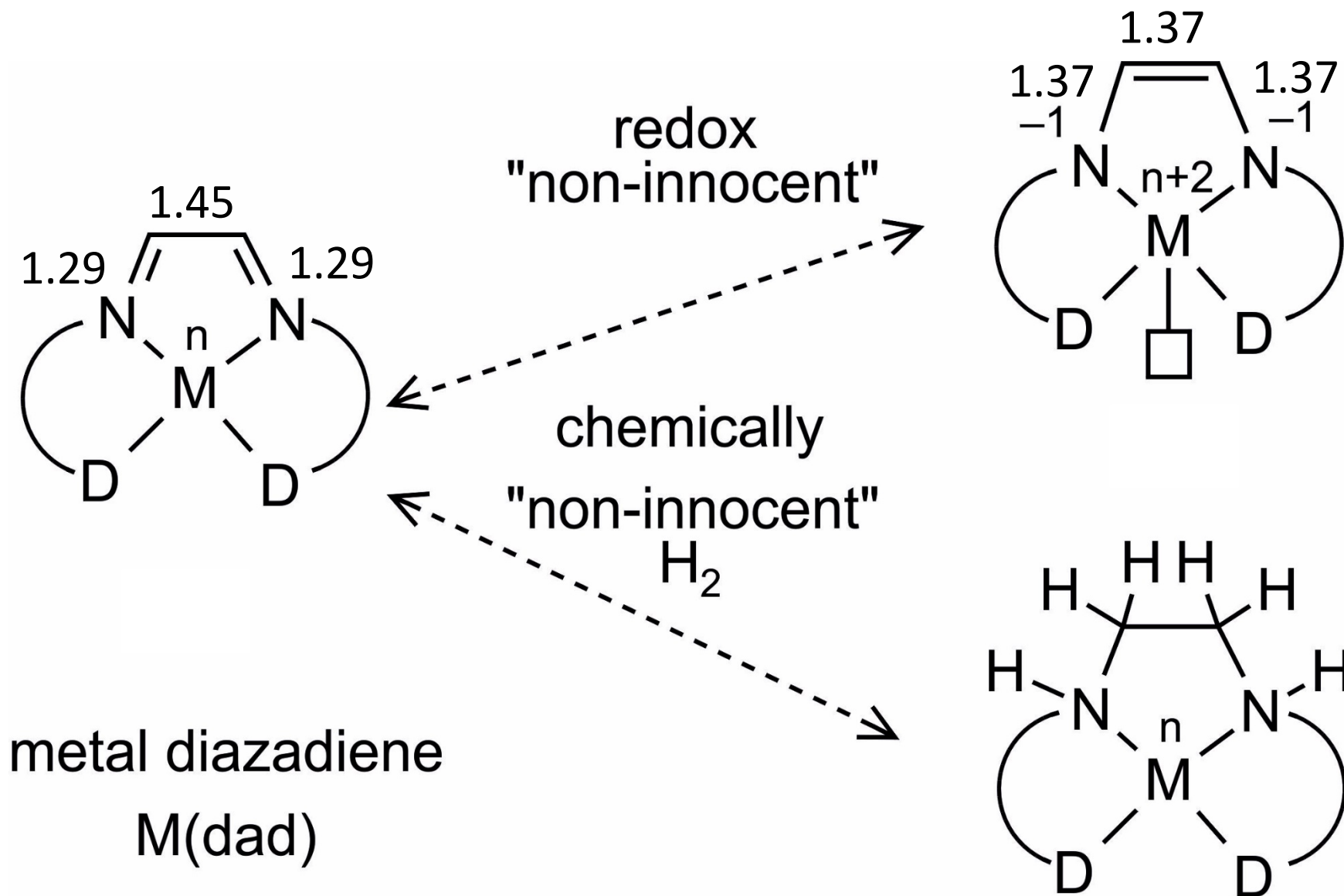
R. M. Navarro, M. A. Pena, J. L. G. Fierro, *Chem. Rev.* **2007**, *107*, 3952.-3991.



12.0 wt% hydrogen; endothermic,

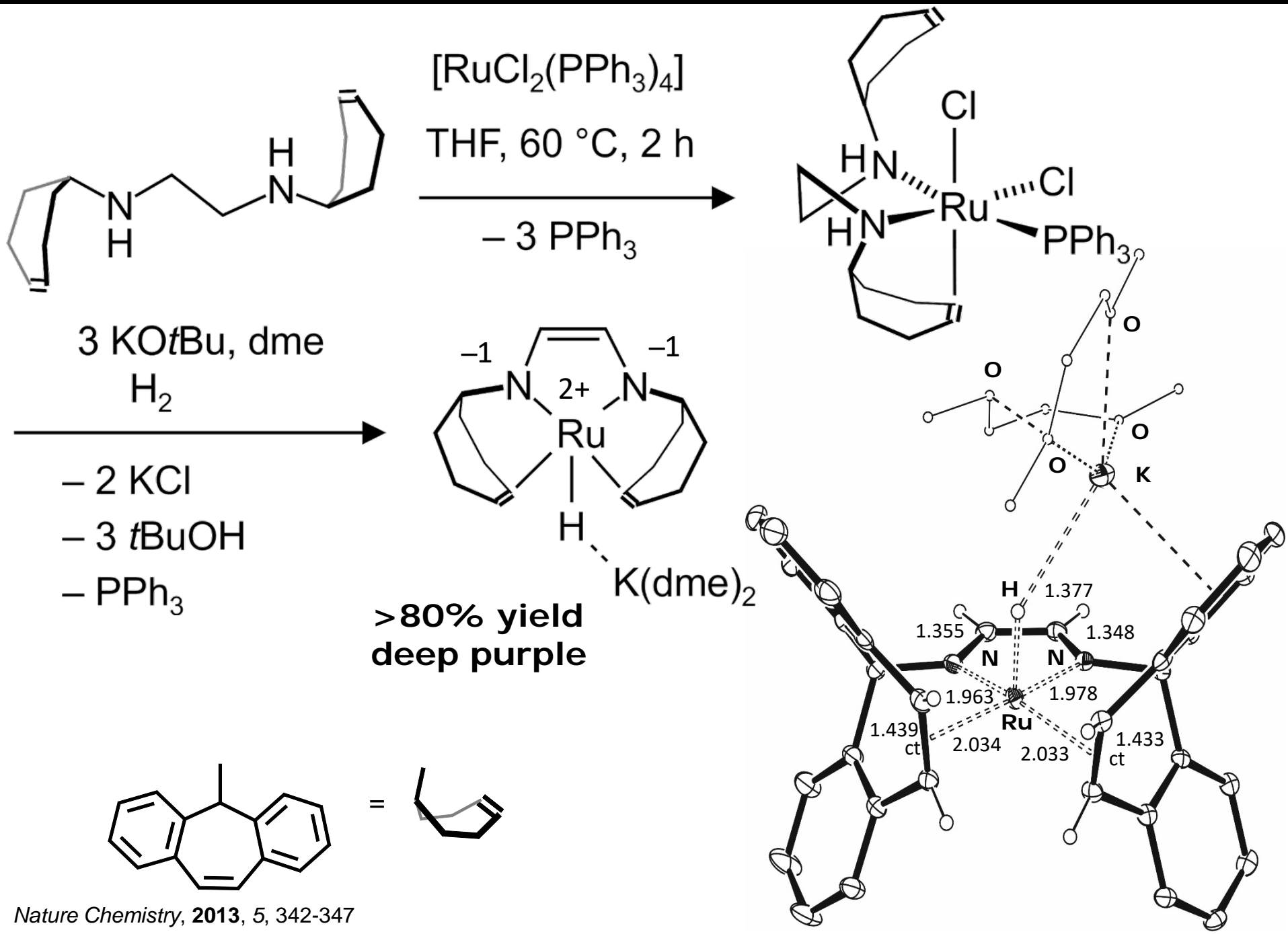


Dad's can be redox and chemically «non-innocent» ligands...

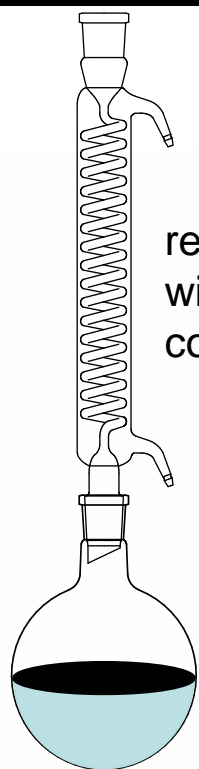


...which can be used for reversible H_2 and/or electron uptake/release.

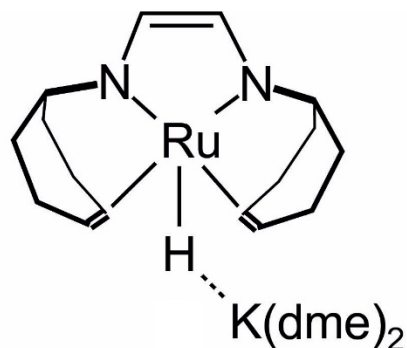
Synthesis of a Ru diazadiene complex under «strange» conditions



Catalytic decomposition of 1:1 MeOH/water mixtures to CO₂ and H₂

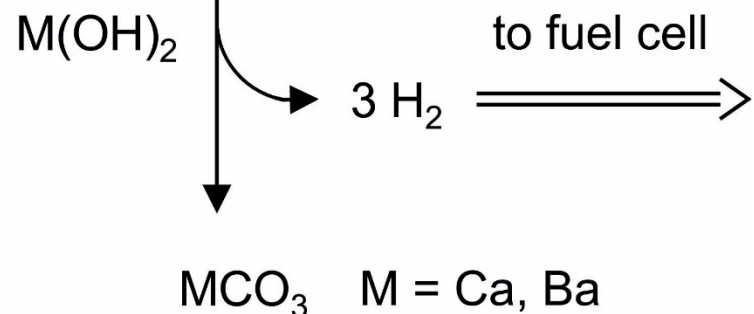
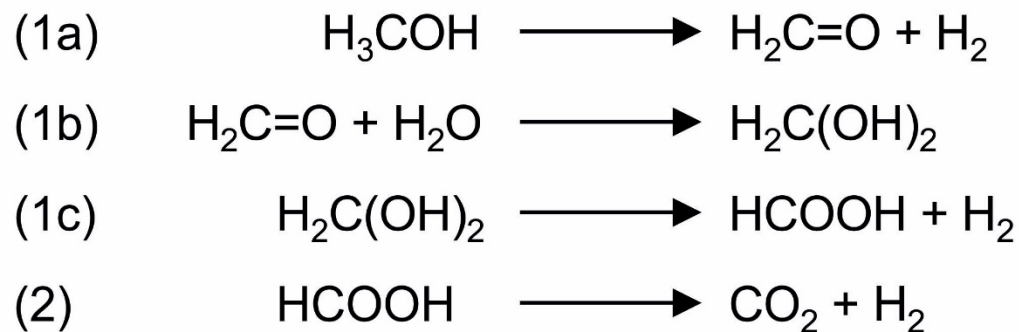
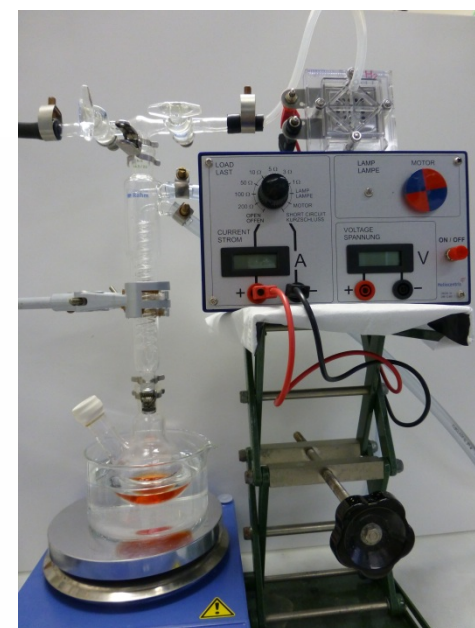
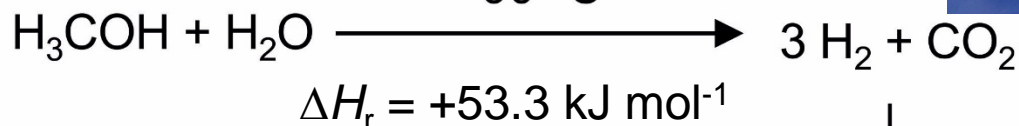


reflux condenser
with circulating
cooling fluid at -20 °C



0.5 mol%

90 °C

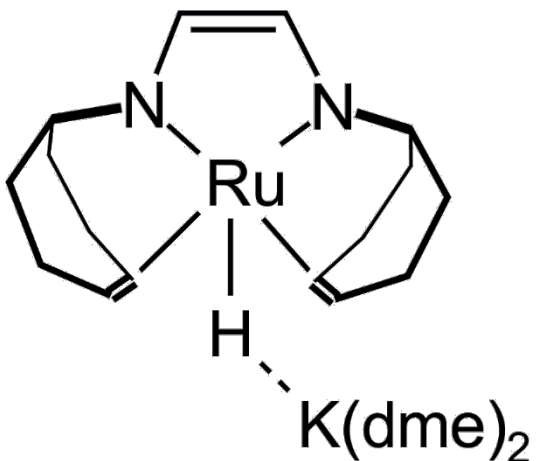


See also:

Beller, Gladiali et al, *Nature*, **2013**, 494, 8

G. Precht, *Nat. Commun.* **2014**, 5, 3621

Catalytic decomposition of formic acid to CO_2 and H_2



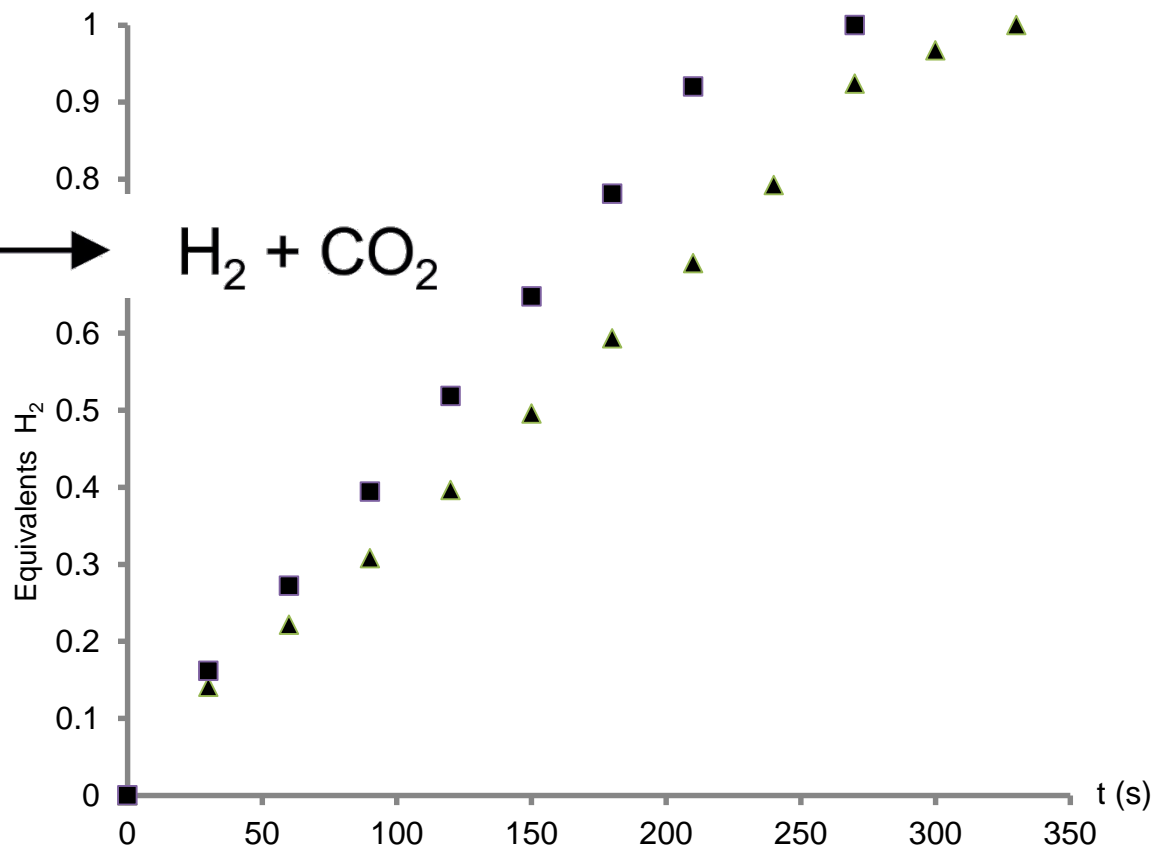
0.01 mol%
90 °C

HCOOH

dioxane

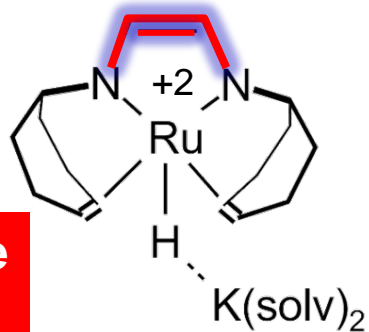
$\text{H}_2 + \text{CO}_2$

TOF > 24'000 h^{-1}

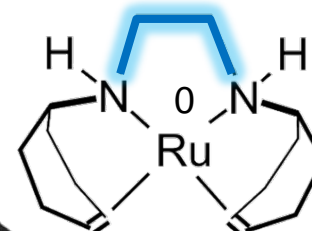
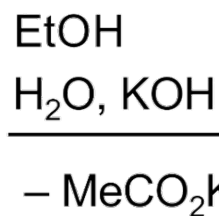
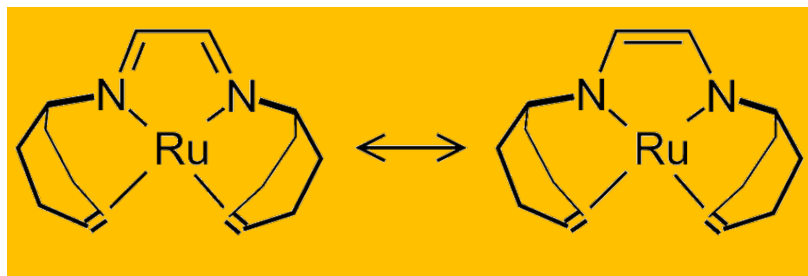
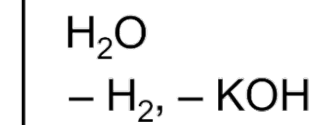


Metal ligand cooperation: Ru(II)(dad) → Ru(0)(dae)

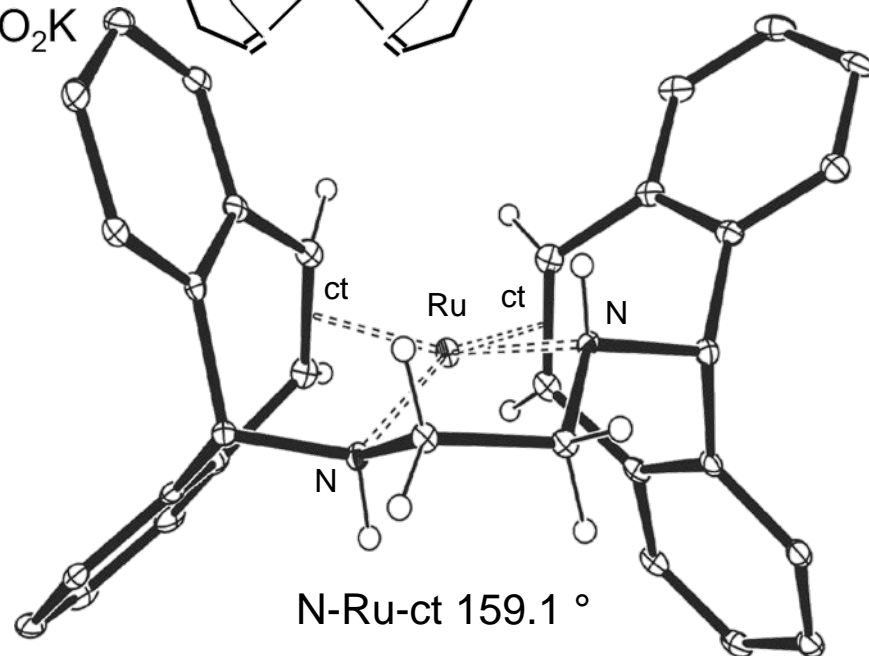
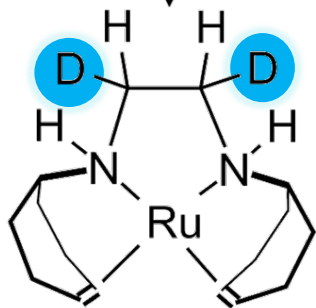
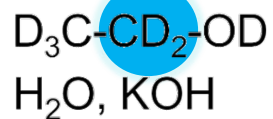
Metal-Ligand Cooperation



**Diazadiene
(dad)**



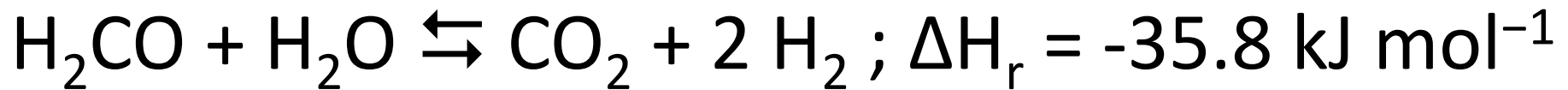
**Diaminoethane
(dae)**



N-Ru-ct 159.1°

Aldehyde Water Shift (AWS) Reaction

Stanley et al, *Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem.* **2004**, 49, 712.

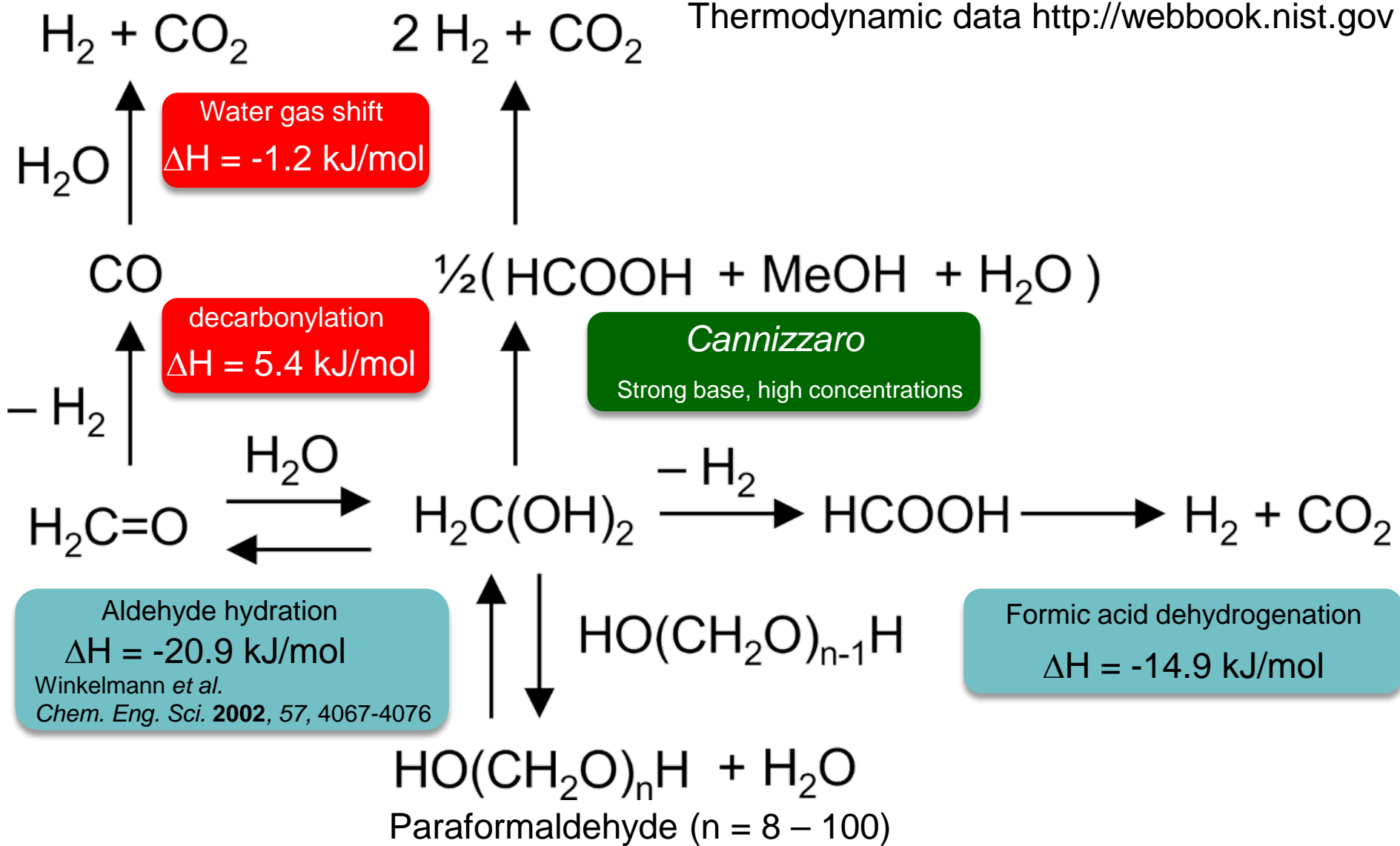


8.3 wt% hydrogen; exothermic

Note: $\text{MeOH} + \text{H}_2\text{O} \rightleftharpoons 3 \text{H}_2 + \text{CO}_2$ is endothermic ($\Delta H_r = 53.3 \text{ kJ mol}^{-1}$)

Formaldehyde is a tricky substrate as hydrogen source....

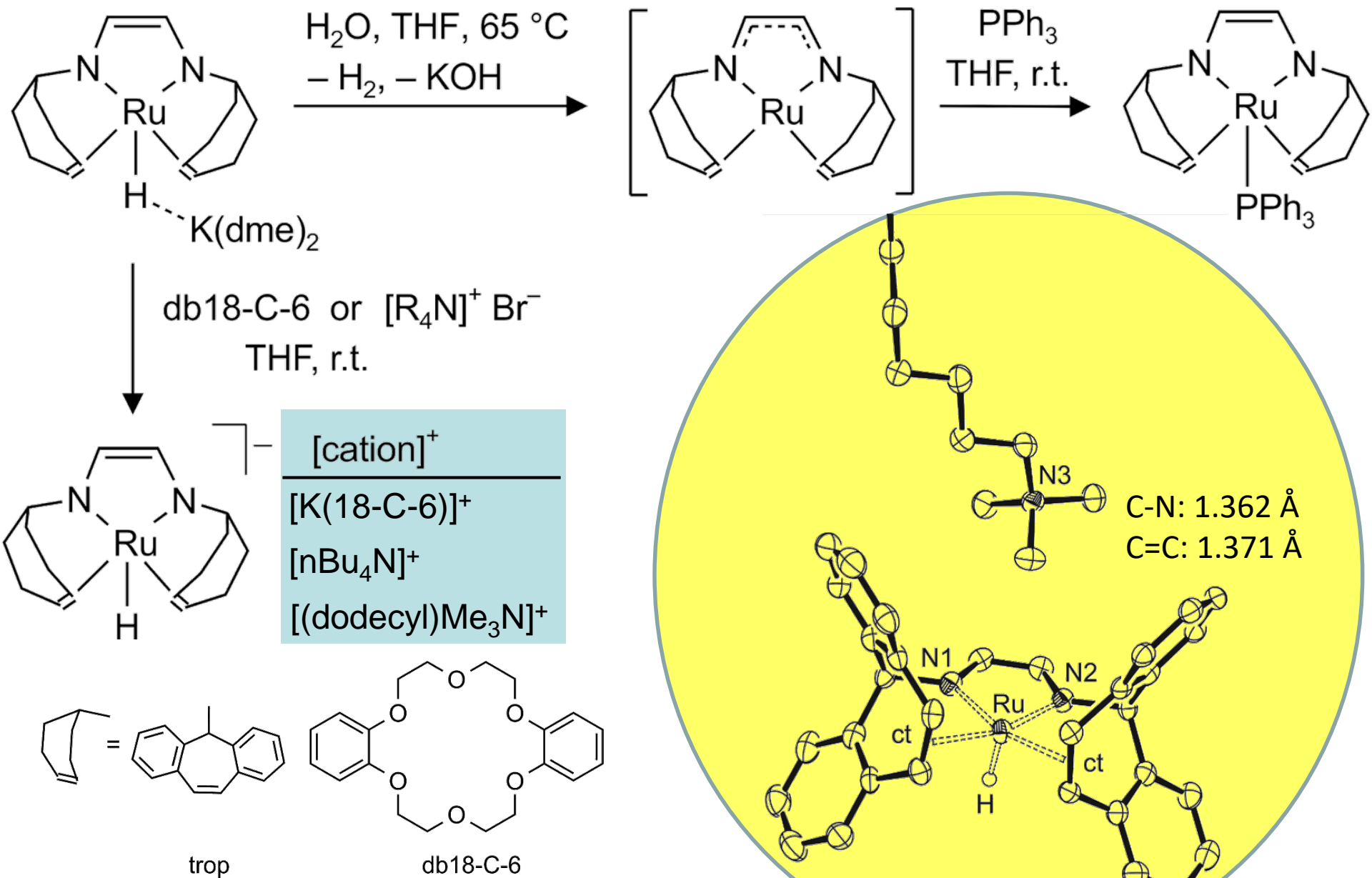
Thermodynamic data <http://webbook.nist.gov>

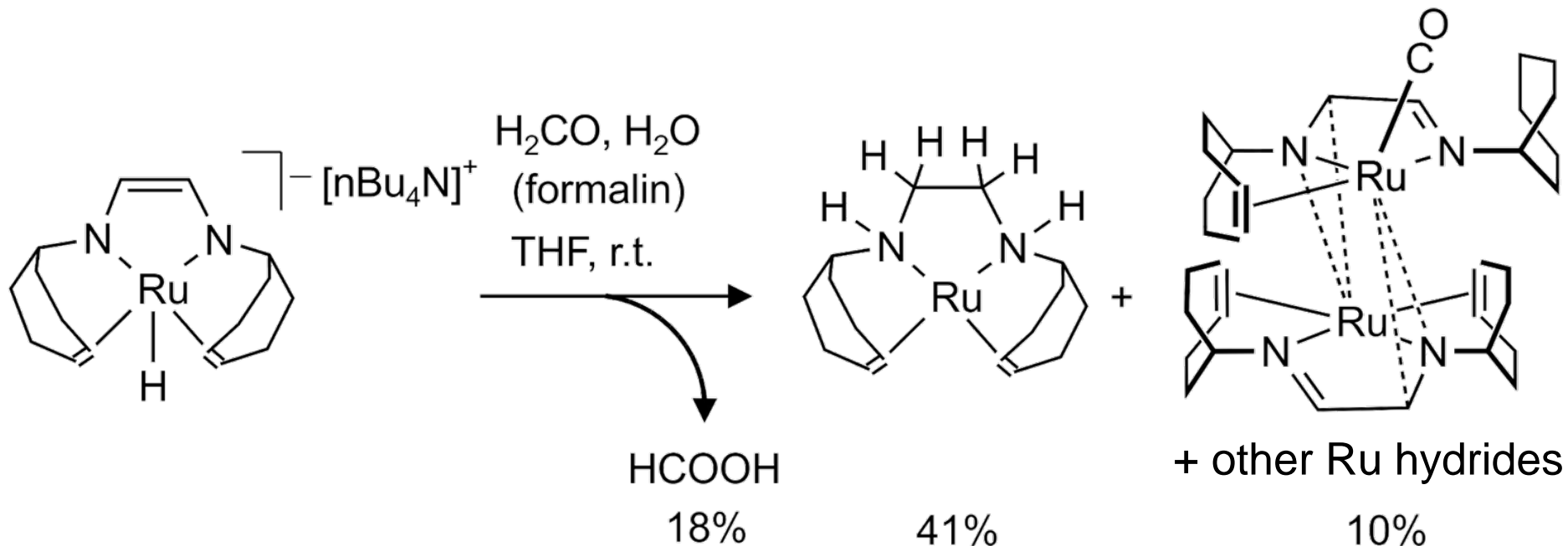


K is strongly T and pH dependent

Maurer et al. *Ind. Eng. Chem. Res.* **1991**, *30*, 2195-2200

Synthesis of AWS catalysts...





Ru^{2+}

redox

Ru^0

N-CH=CH-N

«guilty» ligand

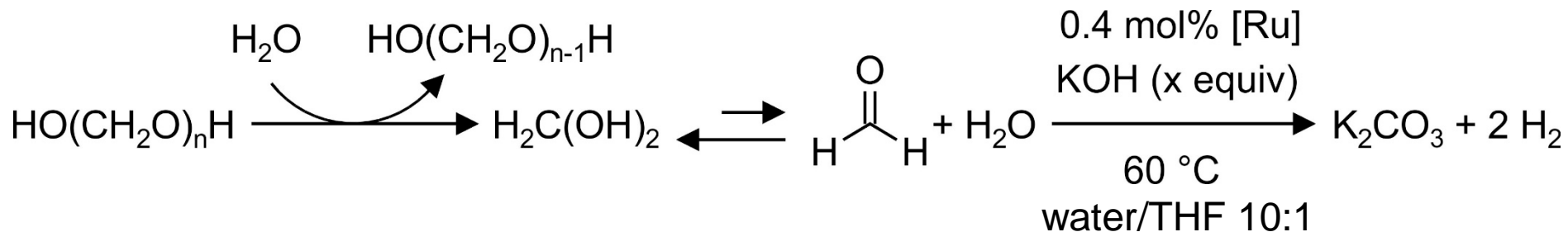
$\text{NH-CH}_2\text{-CH}_2\text{-NH}$

possible complications

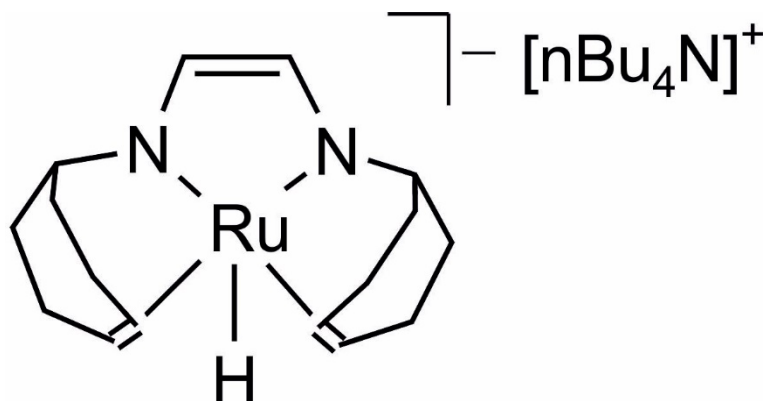
C=C hydrogenation

C=N hydrogenation

decarbonylation



best catalyst

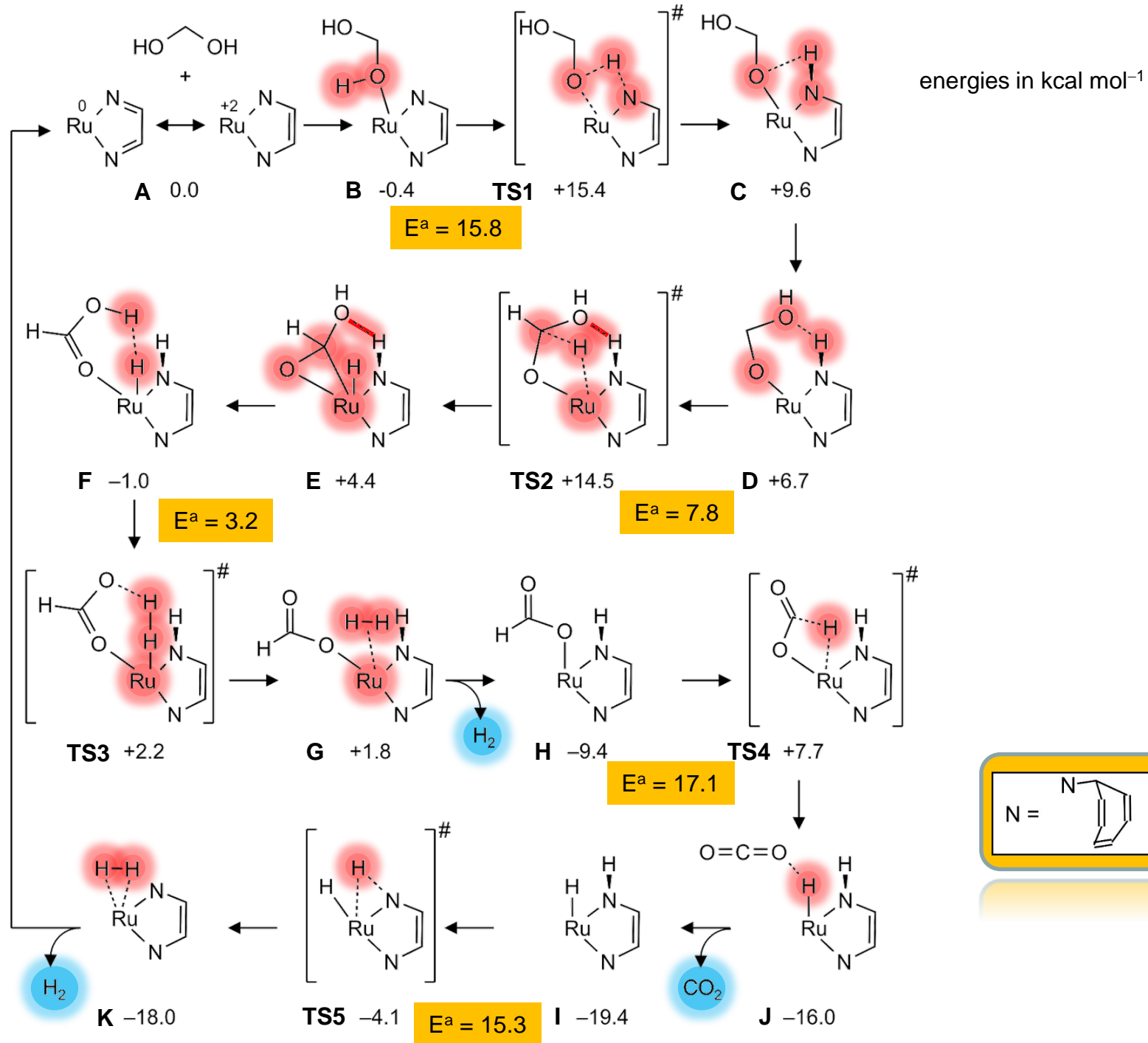


recyclable

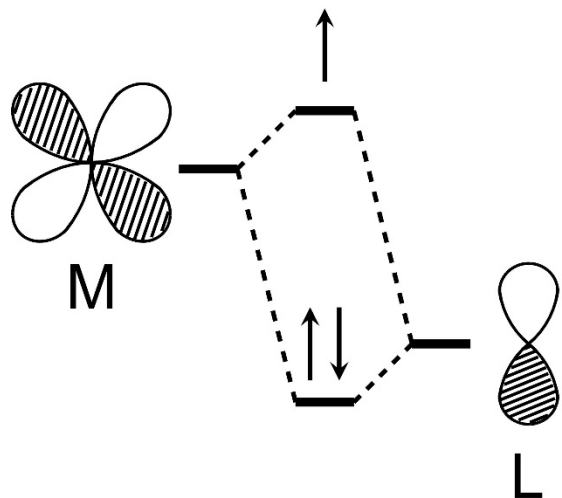
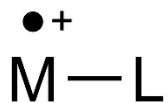
TOF > 20'000 h⁻¹

TON's up to 1800

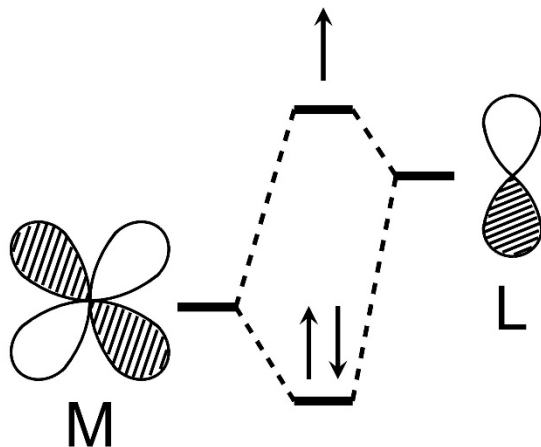
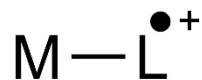
KOH (equiv)	TOF ₅₀ (h ⁻¹)	H ₂ (%) / TON _{max} / time
0	-	23 / 115 / 12 h
6	29'800 (1 ^{rst} run)	90 / 450 / 15 min
6	22'000 (2 nd run)	85 / 765 / 15 min
6 under CO !	805	92 / 460 / 2 h



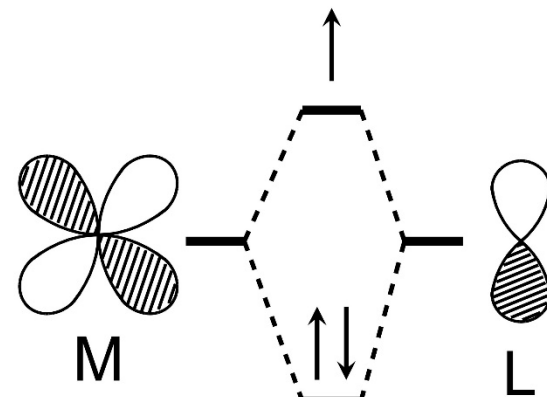
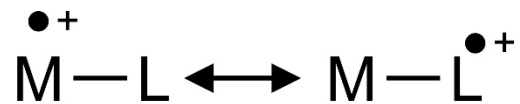
Organometallic Radicals or Metalloradicals?



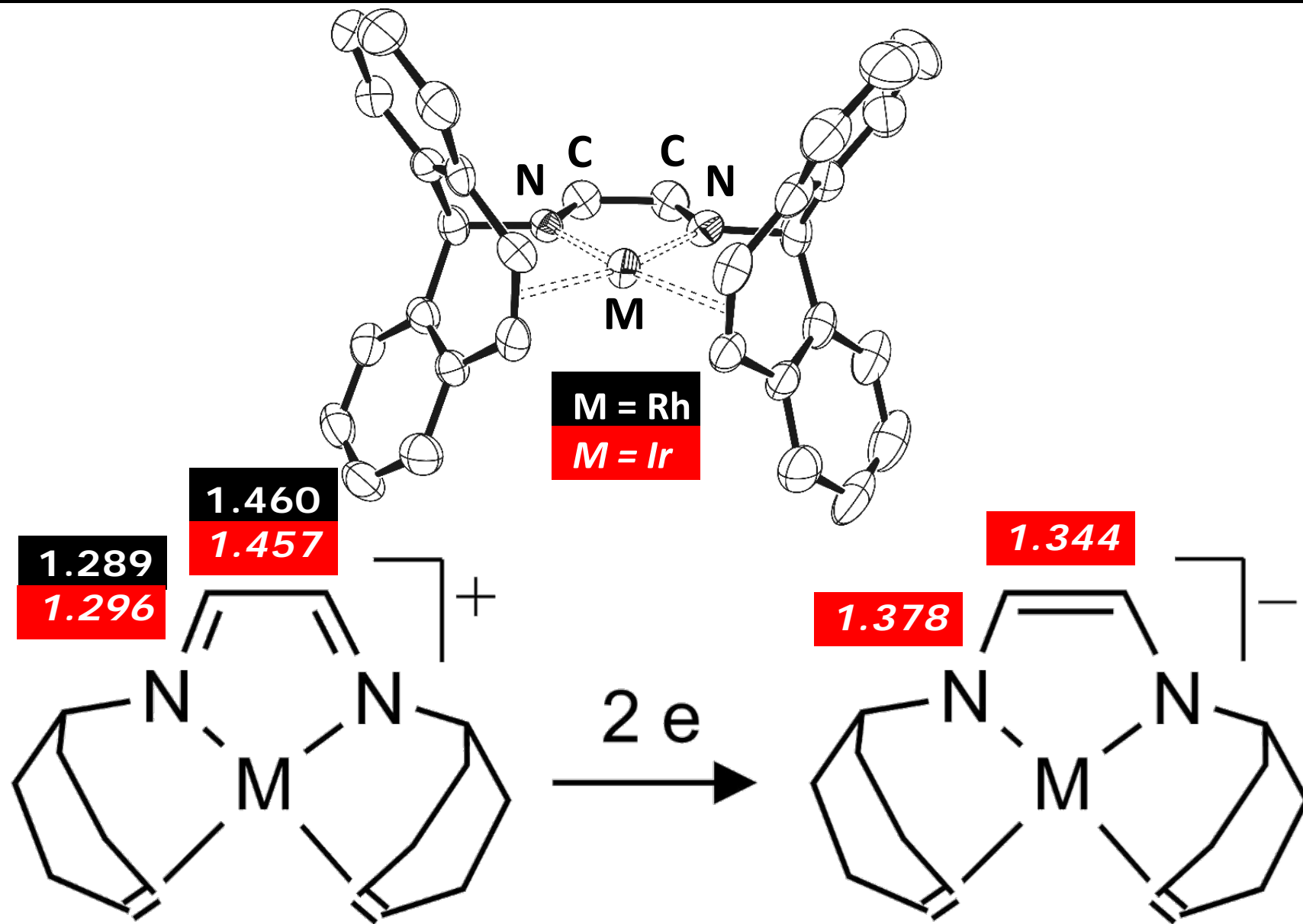
INNOCENT
L



GUILTY
L

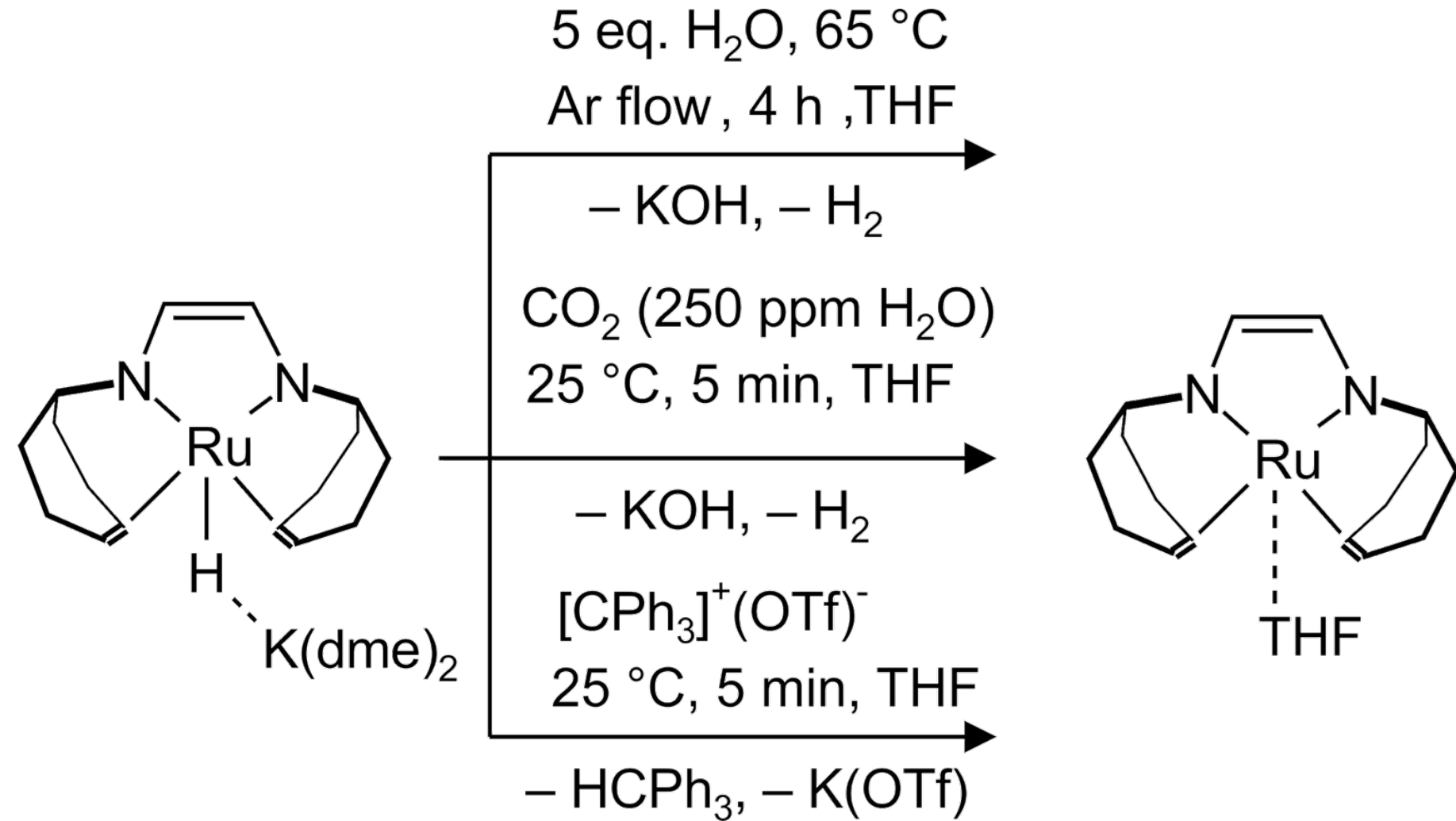


NOT-SO-
INNOCENT
L



Chem. Eur. J. **2003**, *9*, 3859 – 3866.

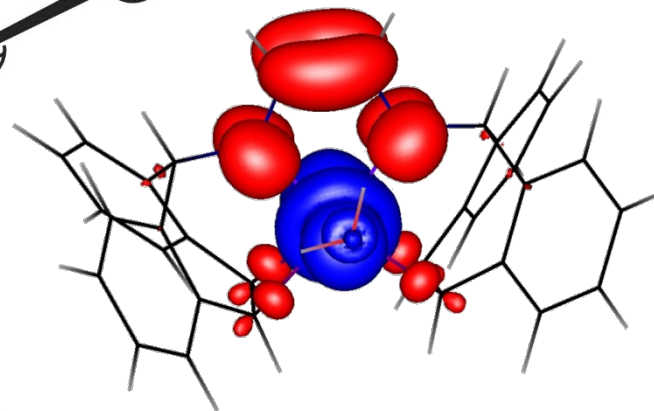
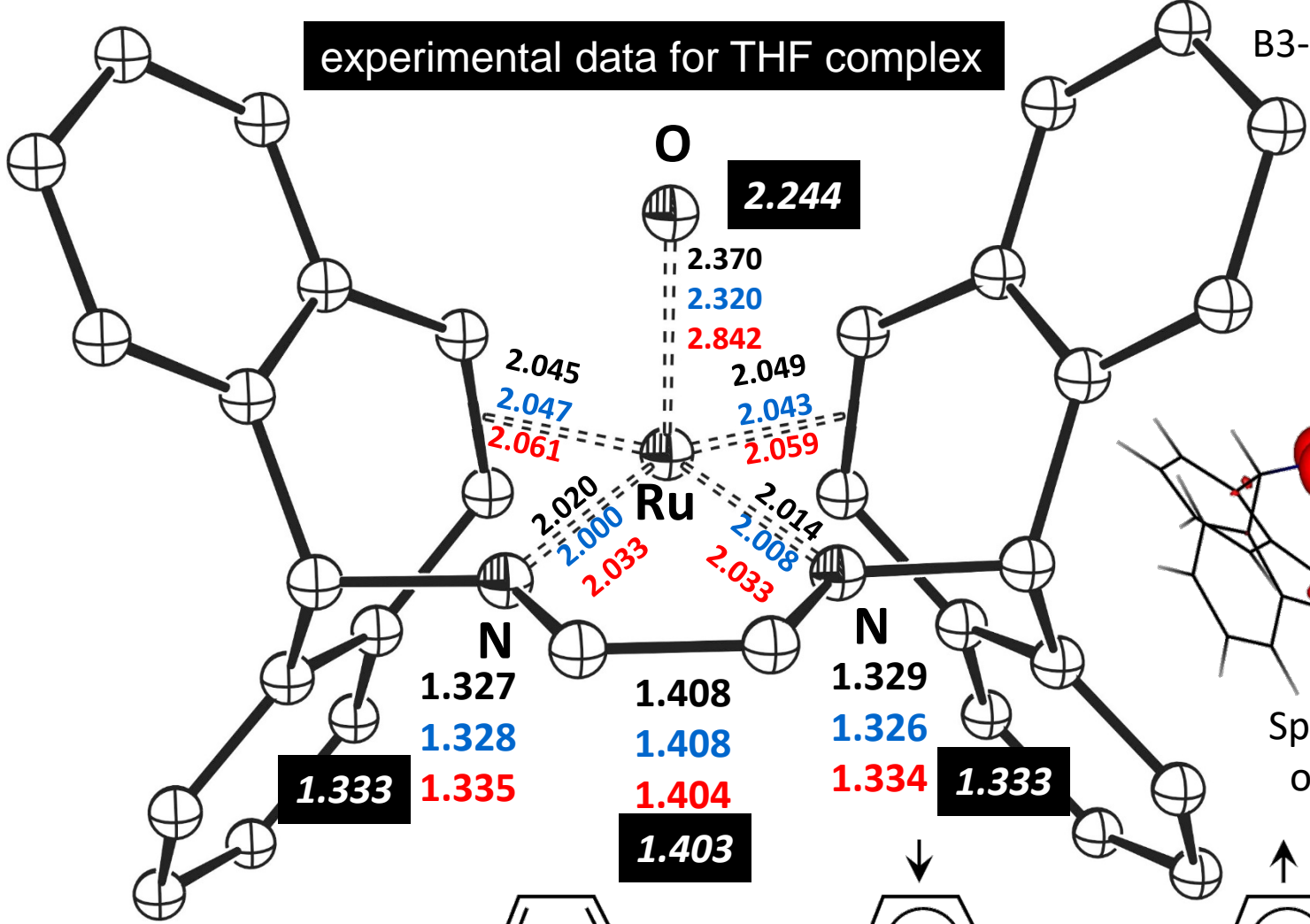
F. Tewes, ETH Diss. No. 18705, 2009.



experimental data for THF complex

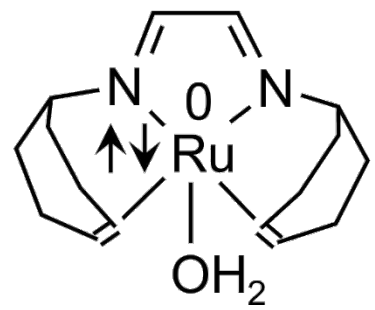
B3-LYP, DEF2-TZVP, DISP3

Monica Trincado,
Bas de Bruin,
unpublished

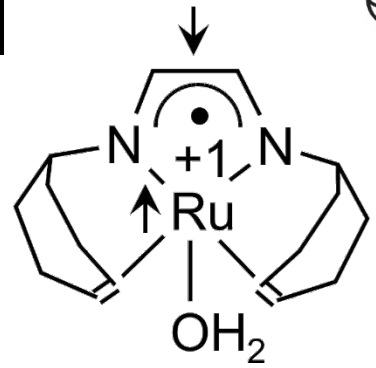


Spin density plot for open-shell singlet

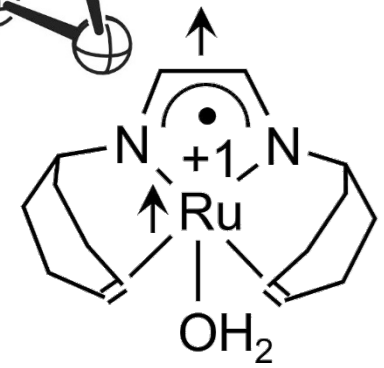
T = 100 K
R1 = 3.69%
reflections to 73°



closed-shell singlet
3.51



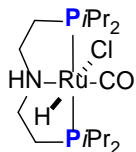
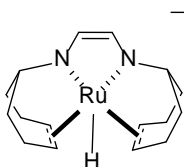
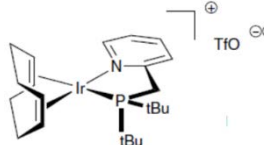
open-shell singlet
0.0

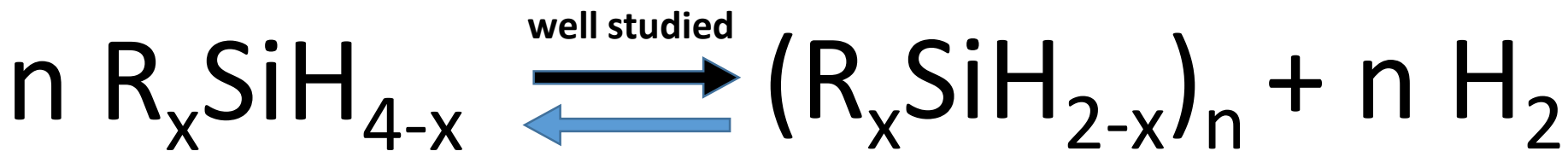


triplet
7.07

kcal mol⁻¹

Potential energy & power densities

		Catalytic dehydrogenation of organic liquid fuels (LOF)/ coupled to H ₂ combustion		
		$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$ $3\text{H}_2 + 3/2 \text{O}_2 \rightarrow 3\text{H}_2\text{O}$	$\text{H}_2\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}_2$ $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$	$\text{HCO}_2\text{H} \rightarrow \text{CO}_2 + \text{H}_2$ $\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$
Energy Density & Power Density of Energy Storage Technologies	Li-ion Batteries (Panasonic 18650)	Catalyst	Catalyst	Catalyst *
		 <p>Beller <i>et al.</i> <i>Nature</i>, 2013, 495, 85</p> <p>TON 353'409 TOF 613 h⁻¹</p>	 <p>Grützmacher <i>et al.</i> <i>Nature Comm.</i> 2017</p> <p>TON 1'787 TOF 12'000 h⁻¹</p>	 <p>Williams <i>et al.</i> <i>Nature Comm.</i> 2016, 7, 11308</p> <p>TON 2'160'000 TOF 13'320 h⁻¹</p>
Specific energy	100–265 W·h/kg (0.36–0.875 MJ/kg)	706 W·h/kg (2.54 MJ/kg)	46.11 W h/kg (0.166 MJ/kg)	1390 W h/kg (5.01 MJ/kg)
Energy density	250–693 W·h/L (0.90–2.43 MJ/L)	575 W·h/L (2.07 MJ/L)	45.80 W h/L (0.165 MJ/L)	1690 W h/L (6.11 MJ/L)
Specific power/ power density	250-340 W/kg	<2 W/Kg (<1 W/L)	230.5 W/kg (229.1 W/L)	<1 W/Kg (<1 W/L)



H₂ content: Ph₂SiH₂ 1.1 %, PhMeSiH₂ 1.6%, Me₂SiH₂ 3.3 %

A. Feigl, A. Bockholt, J. Weis, B. Rieger *Modern Synthetic and Application Aspects of Polysilanes: An Underestimated Class of Materials? In: Muzafarov MA (ed). Silicon Polymers.* (Springer Berlin Heidelberg: Berlin, Heidelberg, **2011**), pp 1-31.

T. Shimoda, *et al.* Solution-processed silicon films and transistors. *Nature* **2006**, *440*, 783-786.

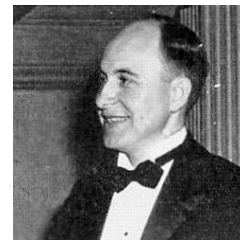
J. F. Harrod *et al.*, Catalytic dehydrocoupling: a general method for the formation of element-element bonds. *Polyhedron* **1991**, *10*, 1239-1245.

J. Y. Corey, Dehydrocoupling of Hydrosilanes to Polysilanes and Silicon Oligomers: A 30 Year Overview. *Adv. Organomet. Chem.* **2004**, *51*, 1-52.

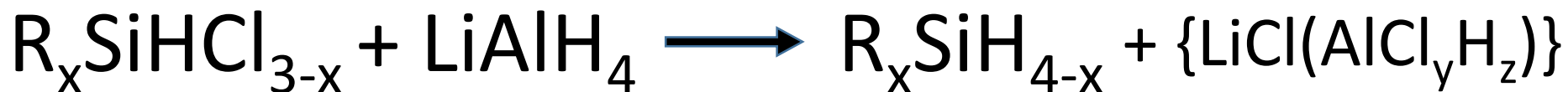
Hydrosilanes are needed as reagents for hydrosilylation, growth of silicon films, formation of silicon carbides.

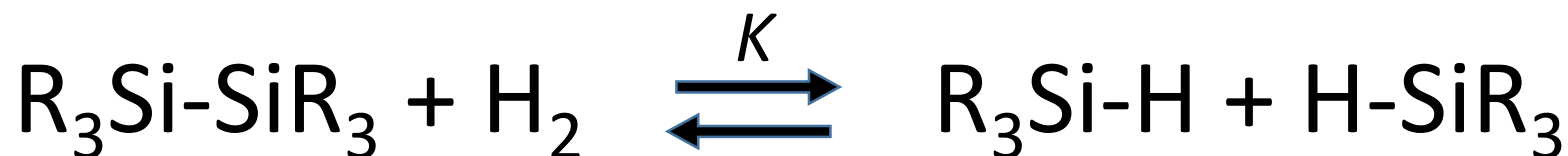


R. Müller, VEB Silikonchemie, DD 5448, (1942);
E. G. Rochow, USP 2380995, (1941);



«high boiling residue»





$$\Delta H_{\text{diss}}(\text{Si-Si}) = 73.1 - 88.0 \text{ kcal mol}^{-1}$$

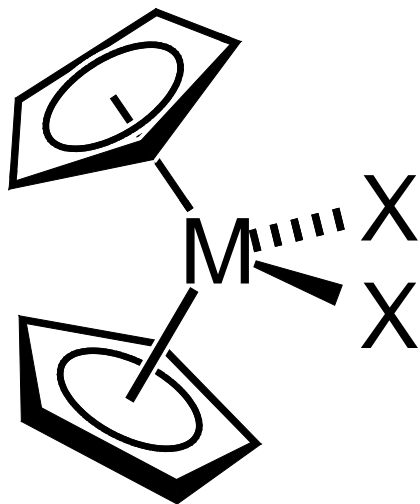
$$\Delta H_{\text{diss}}(\text{Si-H}) > 90 \text{ kcal mol}^{-1}$$

$$K = 10^4 \text{ for } \text{Ph}_2\text{HSi-SiHPh}_2 + \text{H}_2$$

L. Rosenberg et al., *J. Am. Chem. Soc.* **2001**, *123*, 5120–5121.

Y.-R. Luo, *Handbook of bond dissociation energies in organic compounds*.
(CRC Press, Boca Raton, Fla., 2003), pp. 380 p.

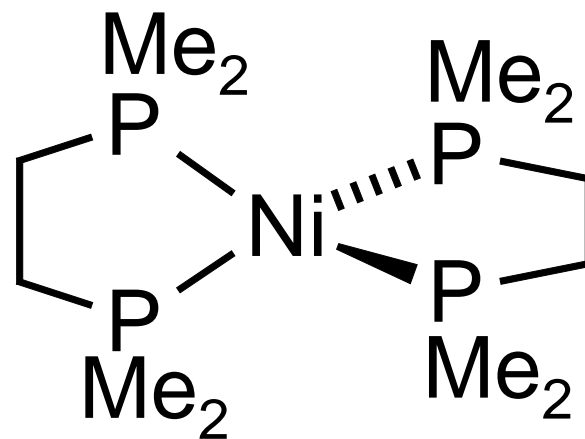
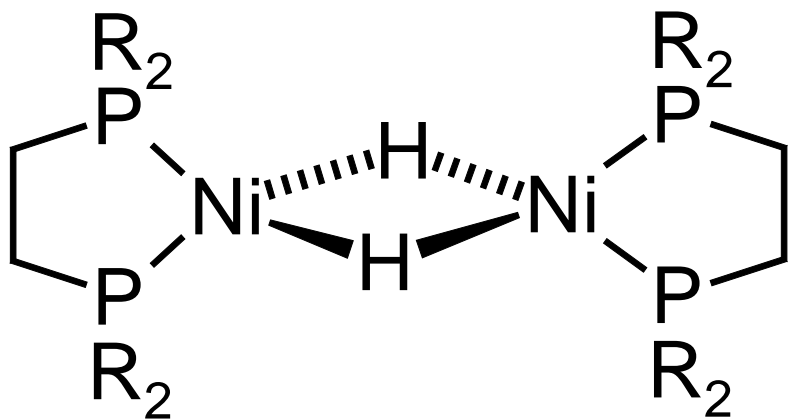
Catalytic dehydrogenation of silanes to polysilanes



classic metallocenes; M = Ti, V

T. D. Tilley, in *The Chemistry of Organic Silicon Compounds*;
Patai, S., Rappoport, Z., Eds., 1989

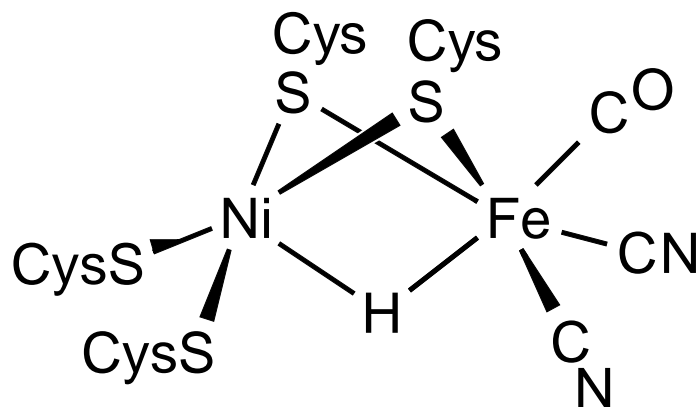
J. Y. Corey. *Chem. Rev.* **2016**, *116*, 11291-11435.



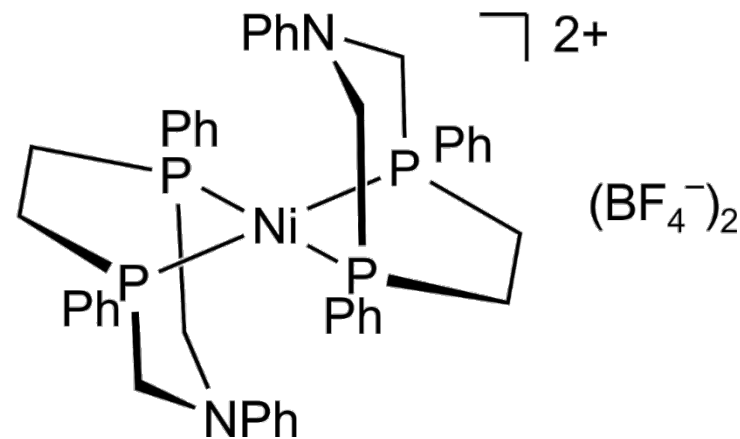
Smith et al., *Organometallics* **2010**, *29*, 6527.

Tanabe et al., *Organometallics* **2013**, *32*, 1037.

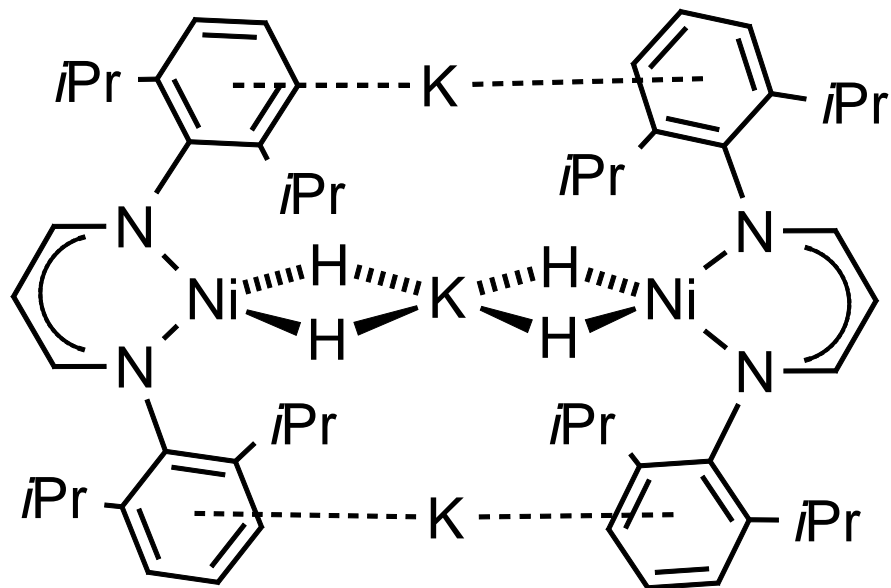
H₂-converting Ni complexes & known low-valent Ni hydrides



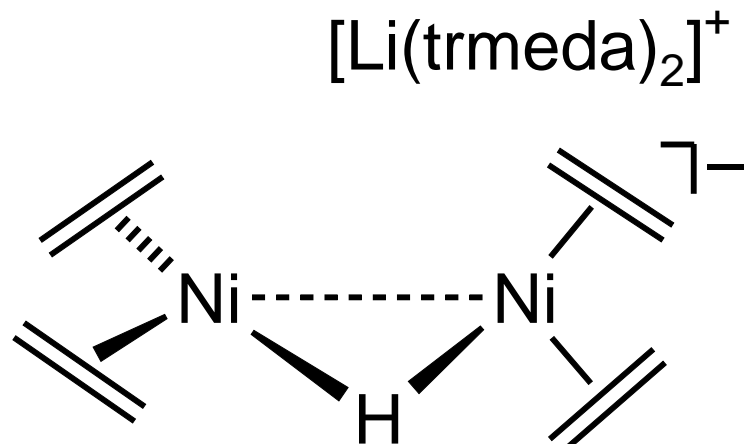
«Mother Nature»
[Ni,Fe] hydrogenase



electrocatalyst with TOF > 100'000 s⁻¹
Bullock, DuBois et al., *Science* **2011**, 333, 863.

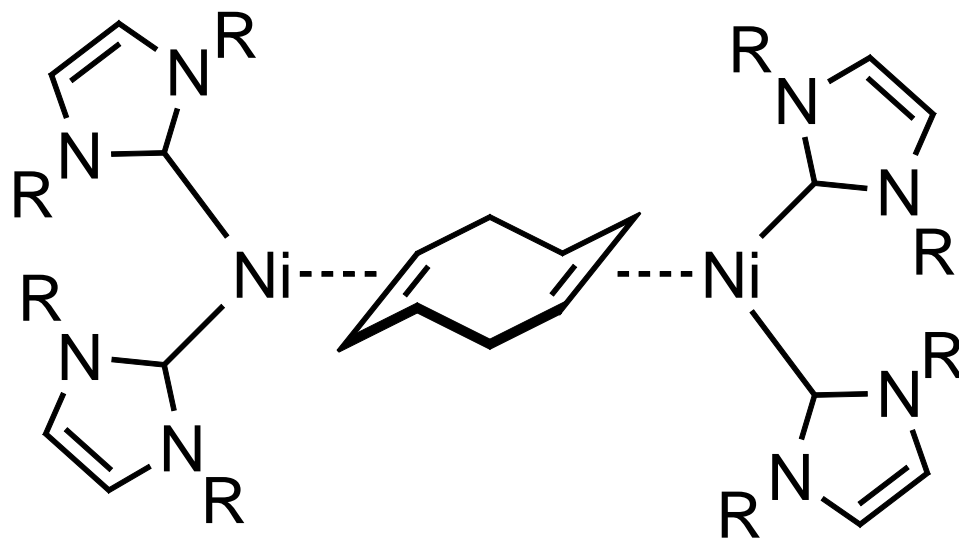
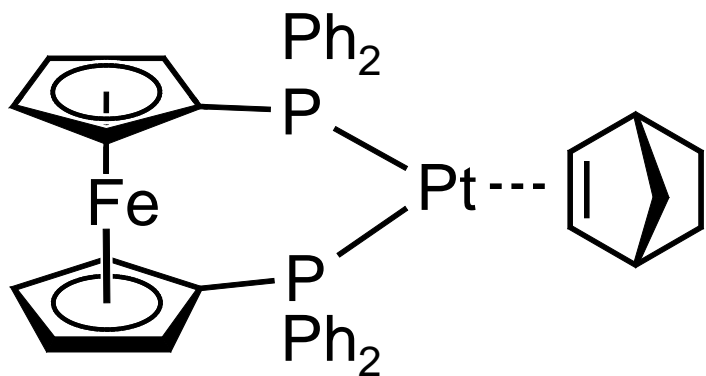


Limberg et al., *J. Am. Chem. Soc.* **2010**, 132, 13684.



K. R. Pörschke et al.,
Angew. Chem. **1983**, 105, 451

Catalytic hydrogenation of disilanes with Pt or Ni complexes,
Long reaction times, TONs up to 20.

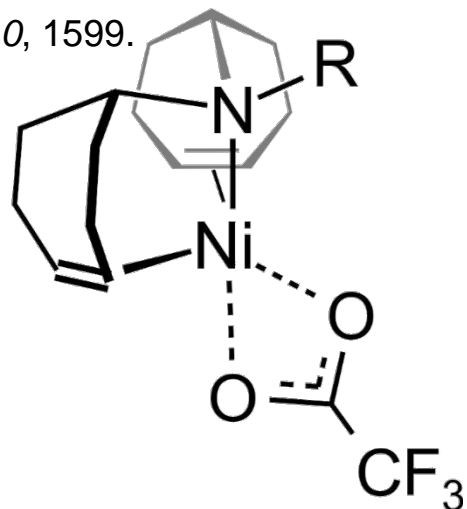
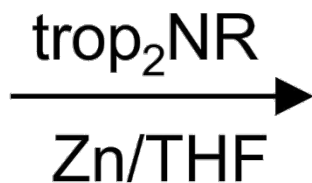
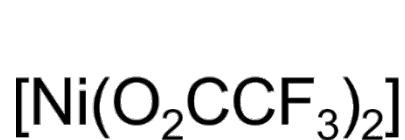


T. Braun et al.,
Eur. J. Inorg. Chem. **2016**, 530-537.

U. Radius et al.,
Dalton Trans. **2014**, 43, 10816.

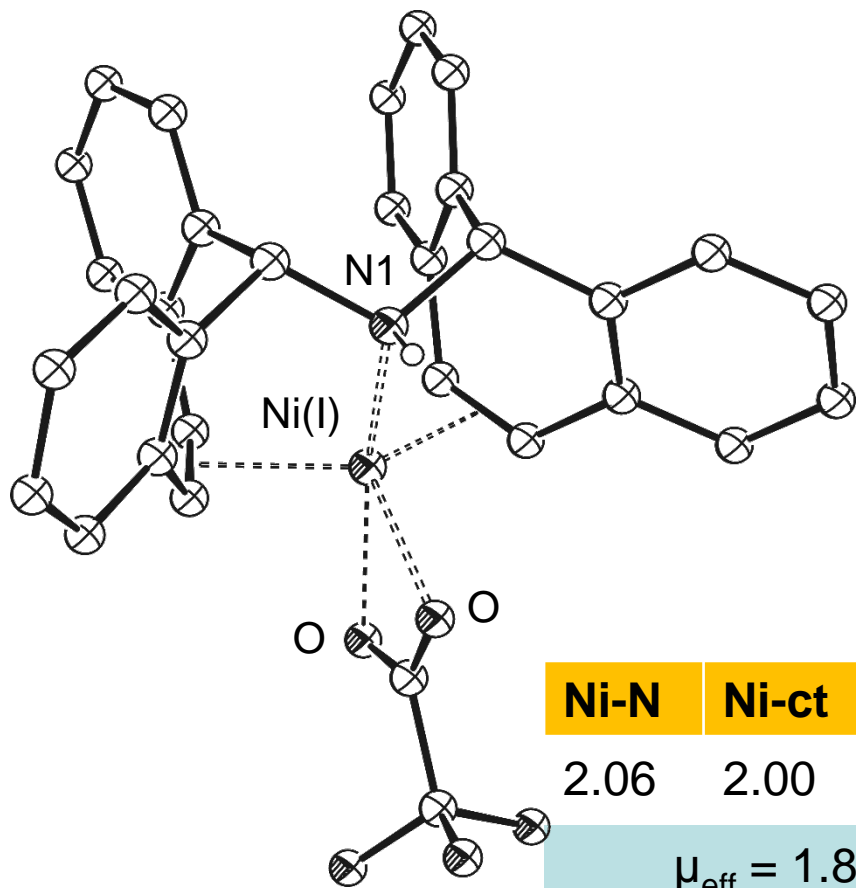
M. Vogt, et al., *Chem. Sci.* **2011**, 2, 723.

M. Trincado, et al., *Eur. J. Inorg. Chem.* **2014**, 10, 1599.



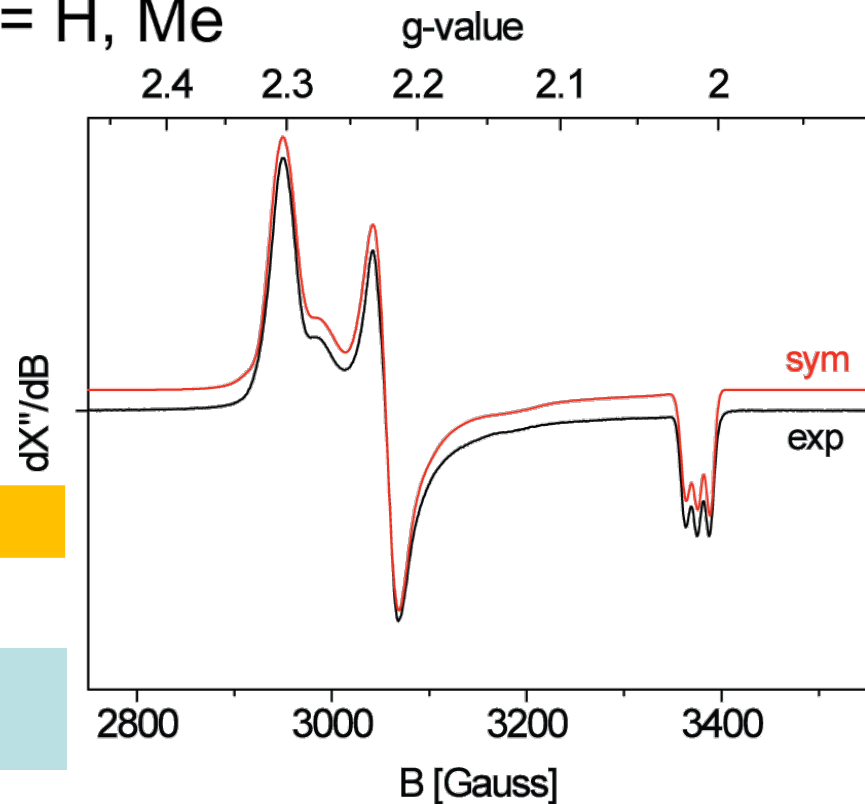
	Exp.	DFT (ORCA)
g_x	2.303	2.225
g_y	2.223	2.169
g_z	2.012	2.028
g_{iso}	2.190	2.141
$\eta^{\text{Ni}} 82\%; \eta^{\text{N}} 10\%$		

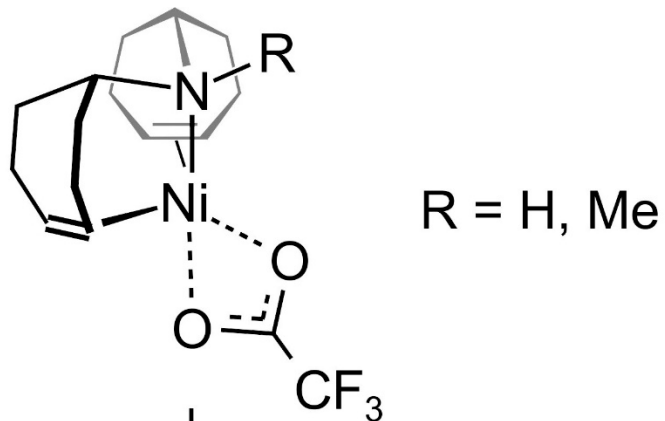
R = H, Me



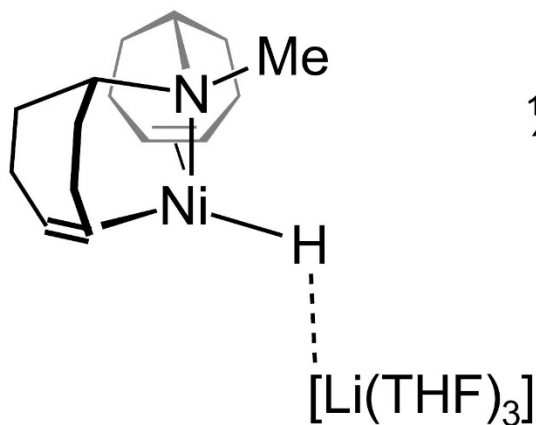
Ni-N	Ni-ct	C=C
2.06	2.00	1.39

$\mu_{\text{eff}} = 1.81 \mu_{\text{B}}$
(SQUID, T = 2 - 300 K)

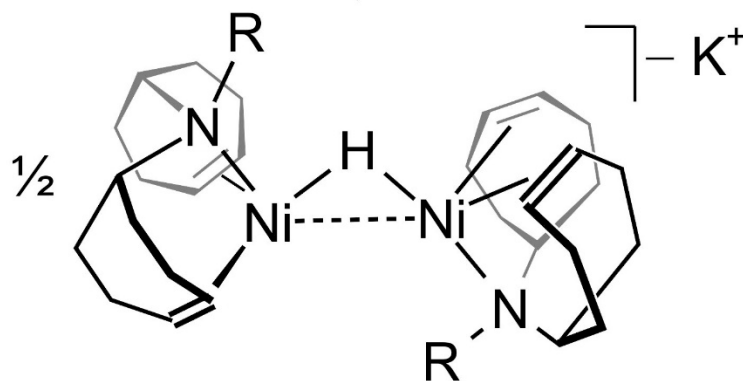


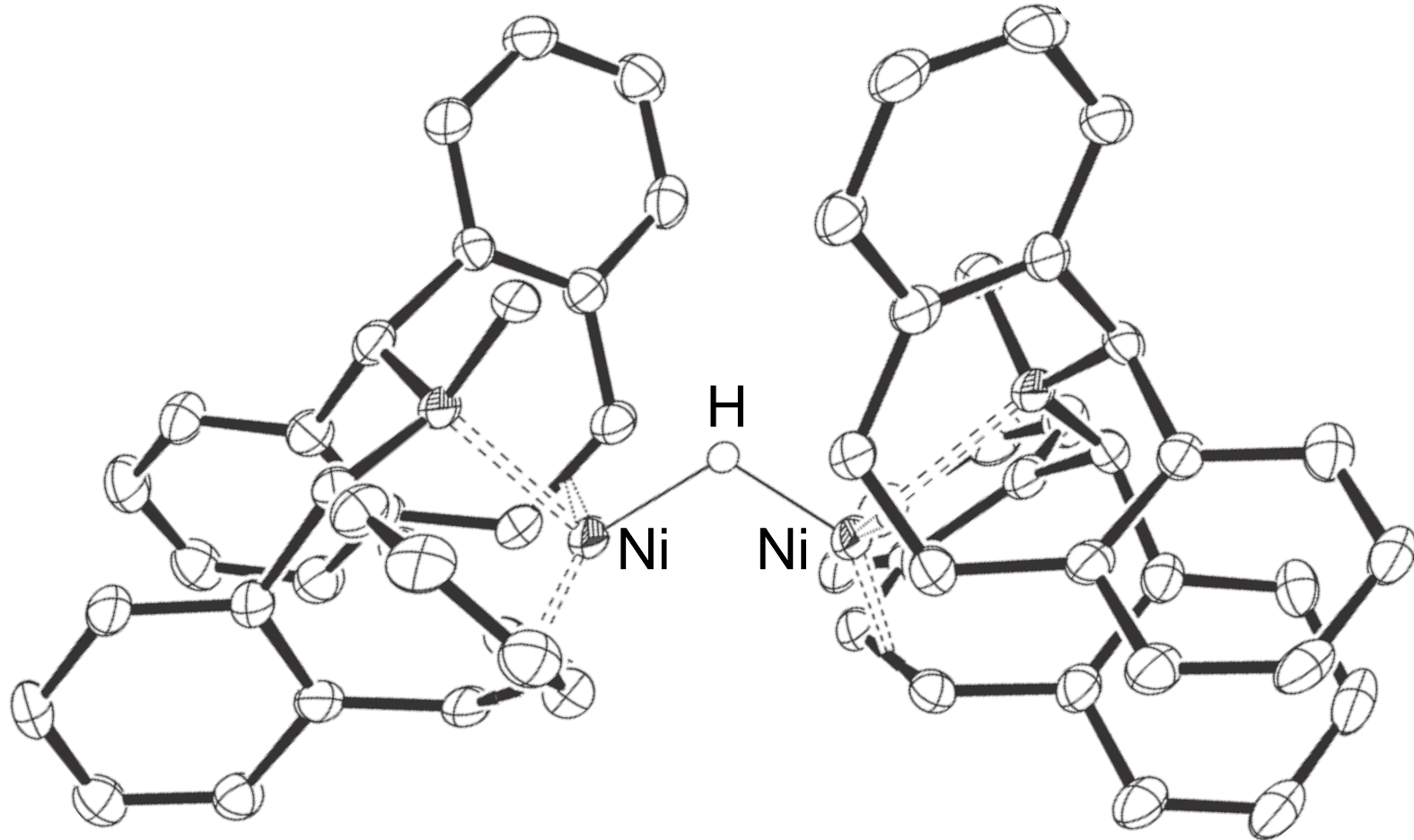


Li[AlH₄] 10 eq.
THF, -30 °C



K[Me₂NBH₃] (1.5 eqv.)
THF, -30 °C
- K(O₂CCF₃)
- H₂ (0.5 eqv.)
- (Me₂NBH₂)₂ (0.75 eqv.)

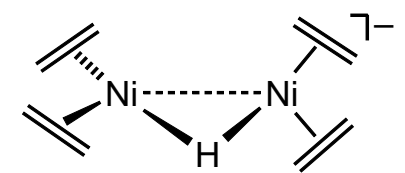




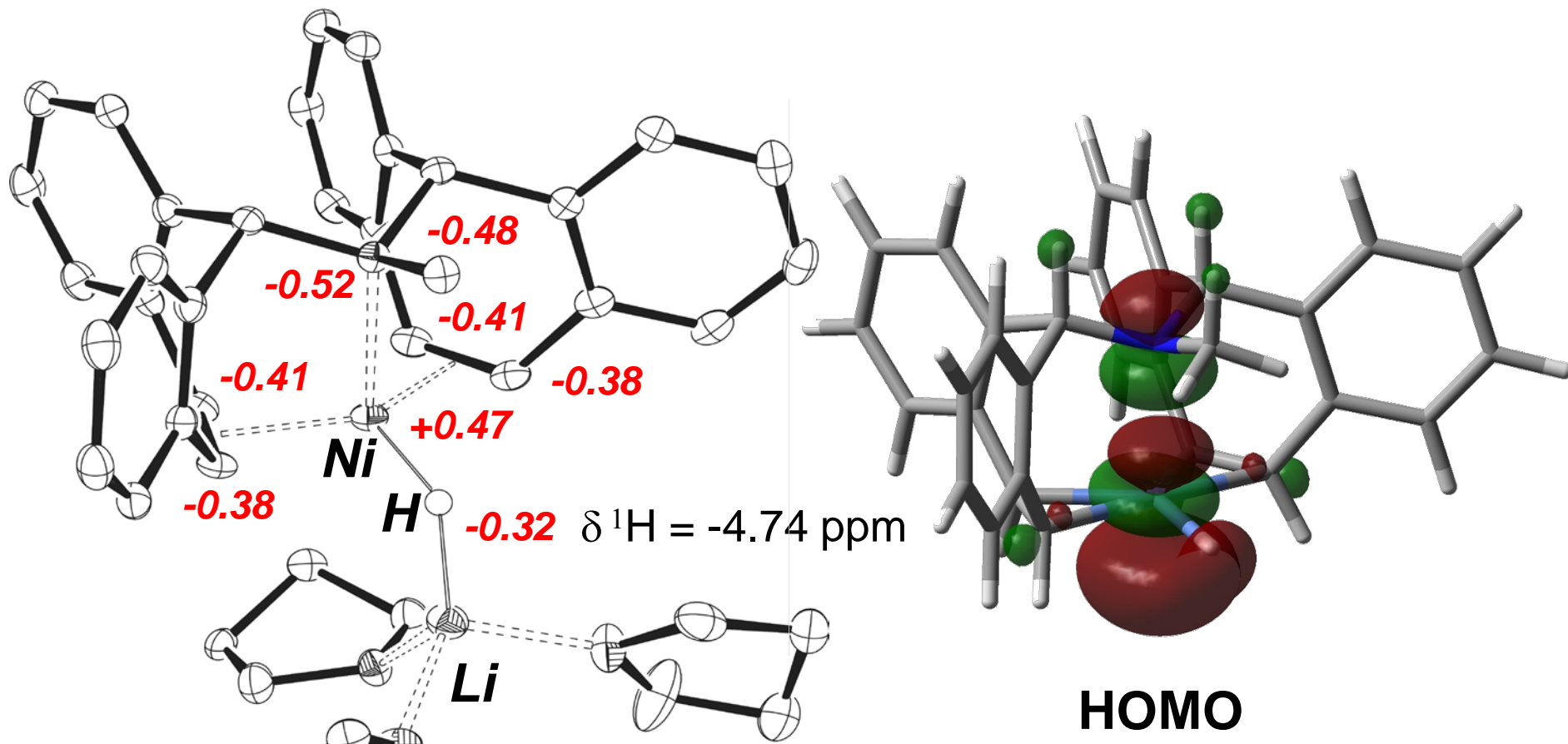
	Ni-N	Ni-H	C=C	Ni...Ni	Ni-H-Ni	$\delta(^1\text{H})$
--	------	------	-----	---------	---------	----------------------

$[\text{Ni}_2(\mu\text{-H})(\text{trop}_2\text{NH})_2]^-$	2.24	1.57	1.41	3.04	151°	-8.12, 1.89 (NH)
---	------	------	------	------	------	---------------------

$[\text{Ni}_2(\mu\text{-H})(\text{trop}_2\text{NMe})_2]^-$	2.24	152, 1.65	1.41	2.76	121°	-6.15
--	------	-----------	------	------	------	-------



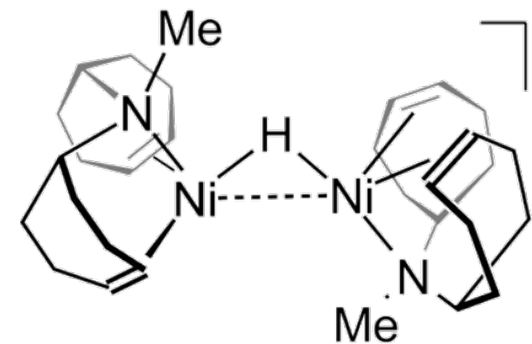
-	-	1.42, 1.52	-	2.596	125°	-
---	---	------------	---	-------	------	---



	Ni-N	Ni-H	C=C	$\delta(^1\text{H})$
$[\text{Ni}^0(\text{H})(\text{trop}_2\text{NMe})]^-$	2.29	1.51	1.42	-4.74
$[\text{Ni}^0(\text{PPh}_3)(\text{trop}_2\text{NR})]$	2.19	—	1.41	—
$[\text{Ni}^{+1}(\text{TFA})(\text{trop}_2\text{NR})]$	2.06	—	1.39	—

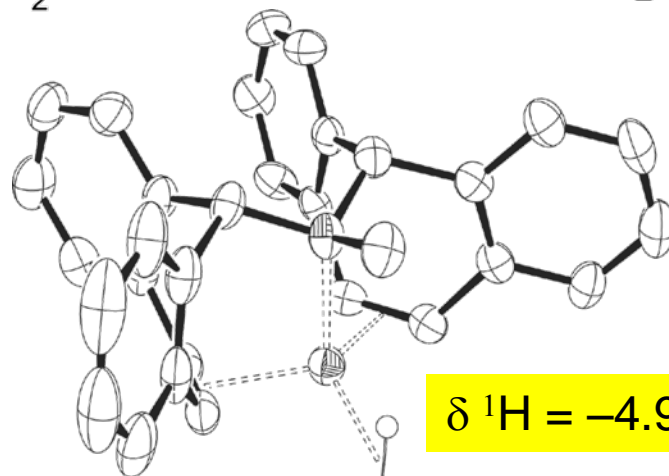
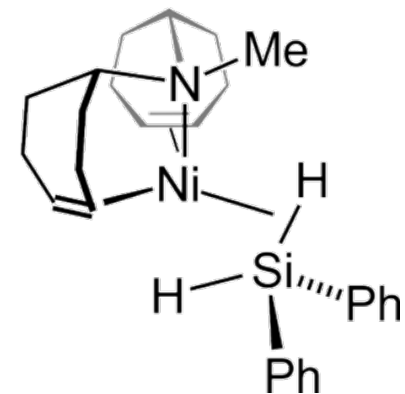
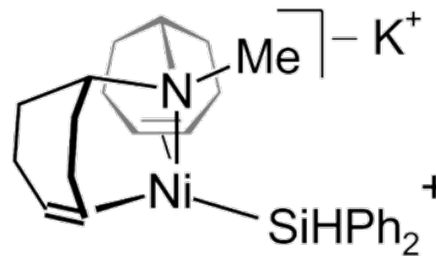
$\text{K}[\text{Me}_2\text{NBH}_3]$
THF, r.t. few min.

$-\frac{1}{2} (\text{Me}_2\text{NBH}_2)_2$
 $-\text{H}_2$



Ph_2SiH_2 (3 eqv.)
THF, r.t.

$-\text{H}_2$



$\delta \text{ } ^1\text{H} = -4.98 \text{ ppm}$

Ph_2SiH_2

$\delta \text{ } ^1\text{H} = 4.94 \text{ ppm}$

$\delta \text{ } ^{29}\text{Si} = -33.0 \text{ ppm}$

$\delta \text{ } ^1\text{H} = 4.96 \text{ ppm}$

$\delta \text{ } ^{29}\text{Si} = -17.7 \text{ ppm}$

Ni-N

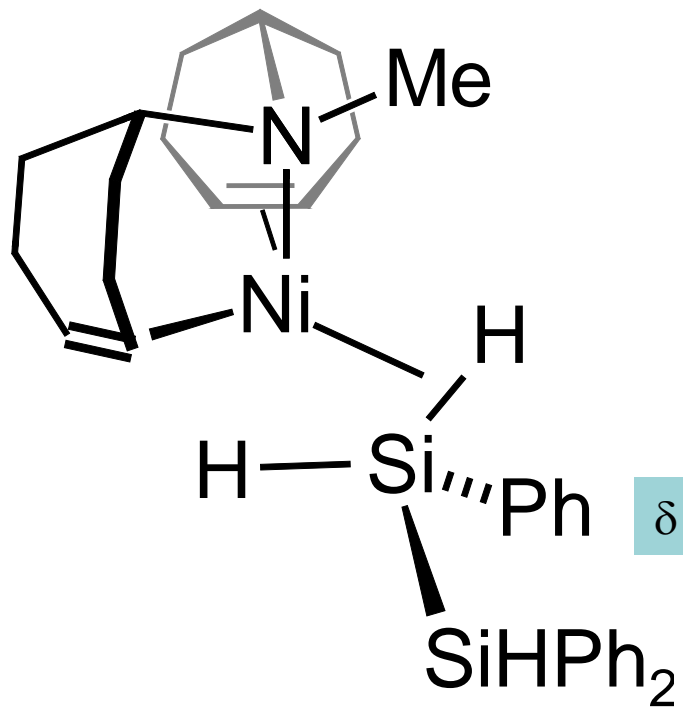
2.12

Ni-Si

2.24

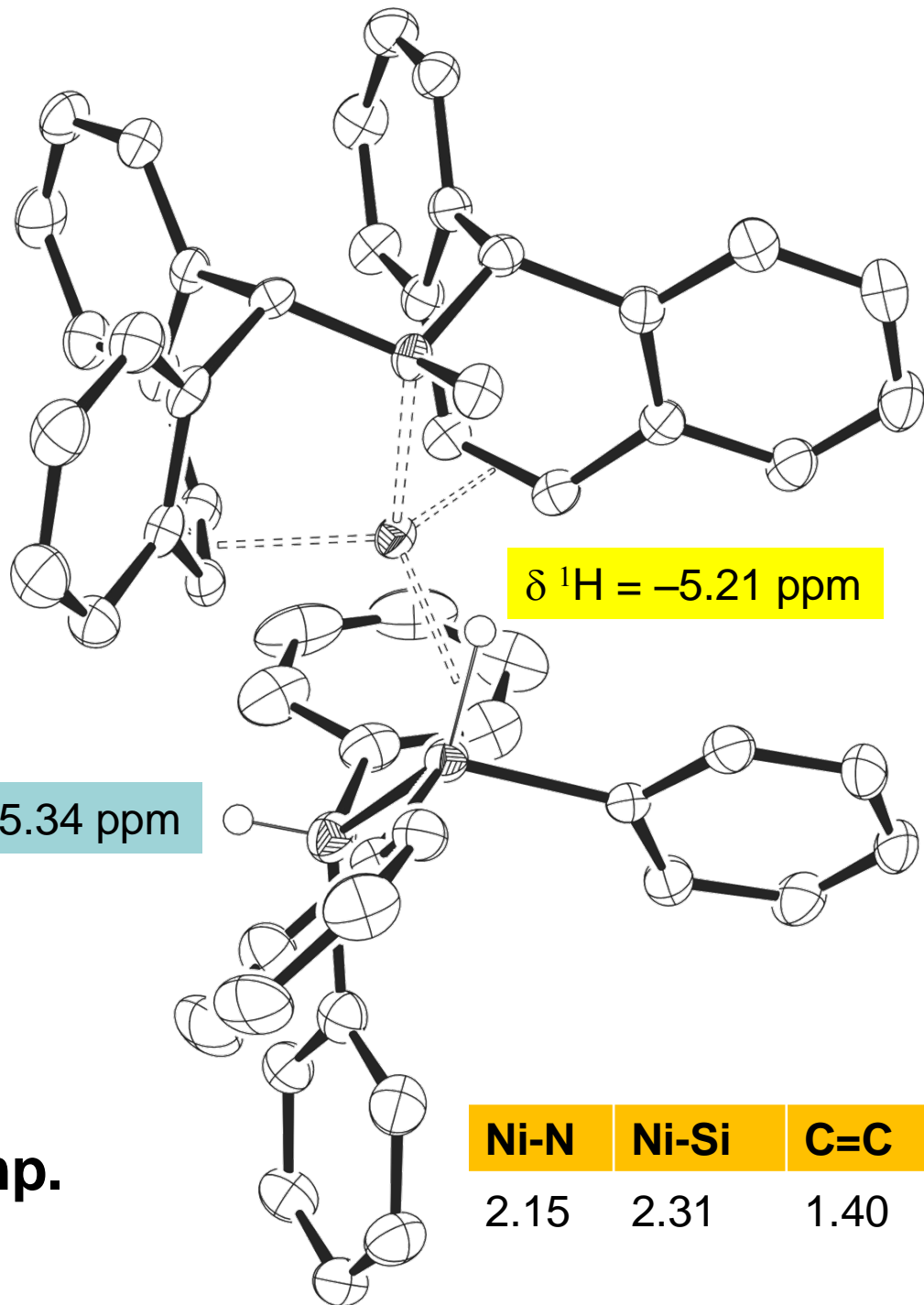
C=C

1.40

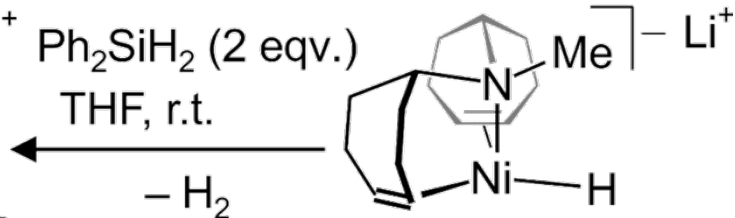
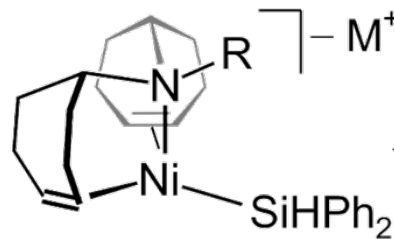
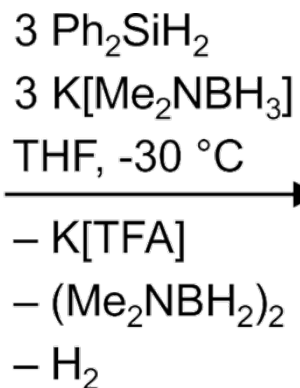
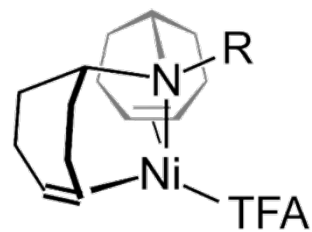


$\delta^1\text{H} = 5.34 \text{ ppm}$

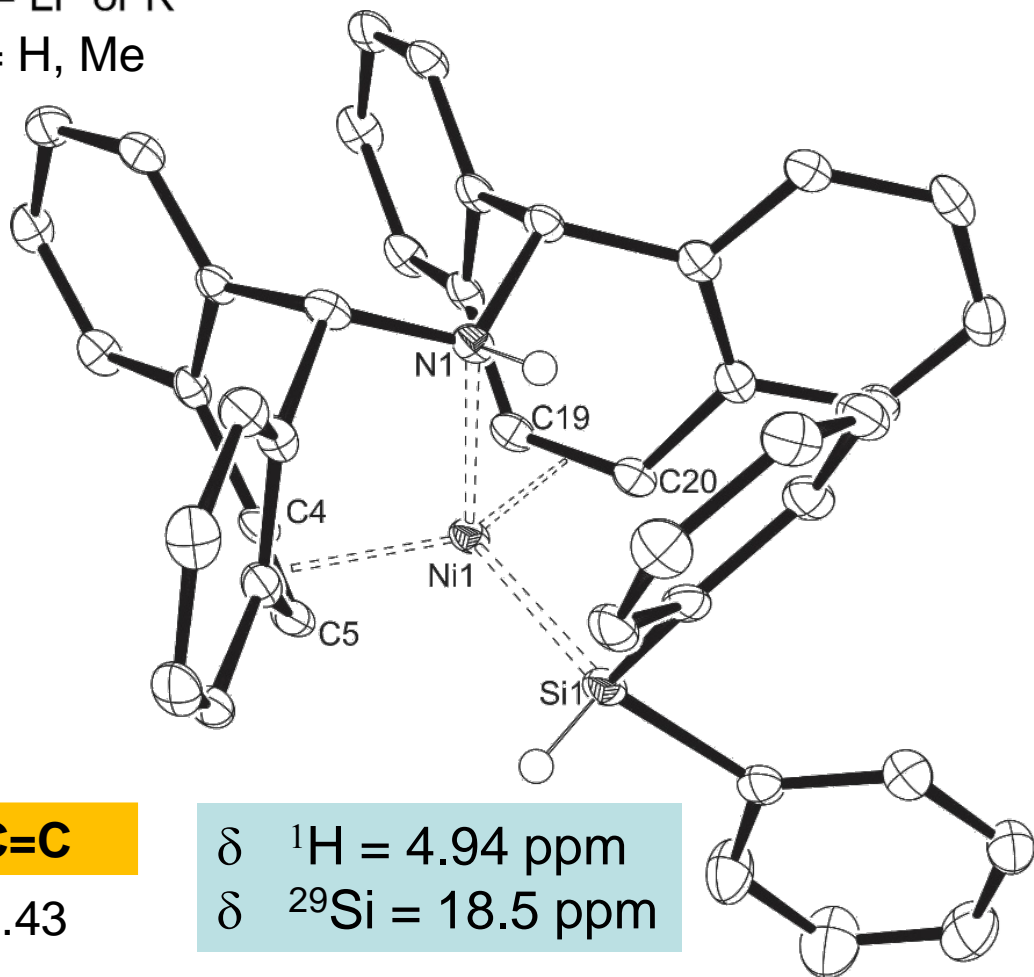
after 5 days, room temp.
30% yield



Ni-N	Ni-Si	C=C
2.15	2.31	1.40

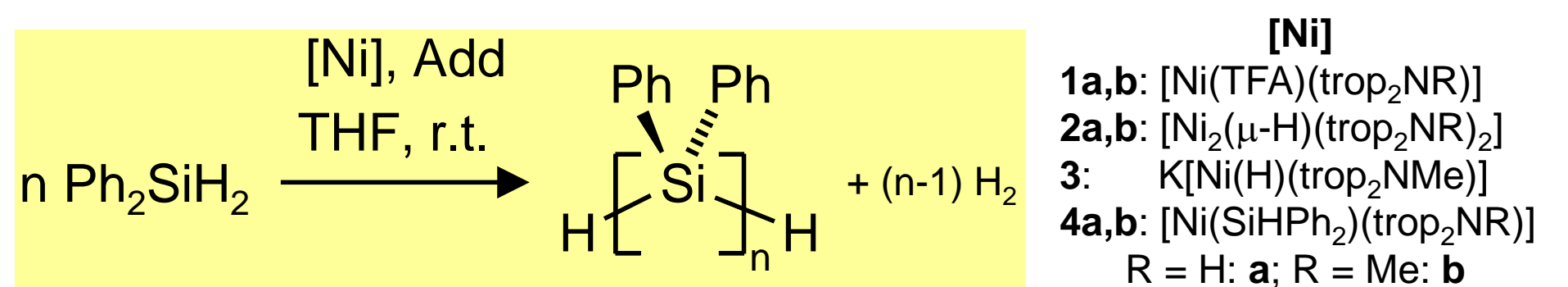


$\text{M}^+ = \text{Li}^+ \text{ or } \text{K}^+$
 $\text{R} = \text{H, Me}$



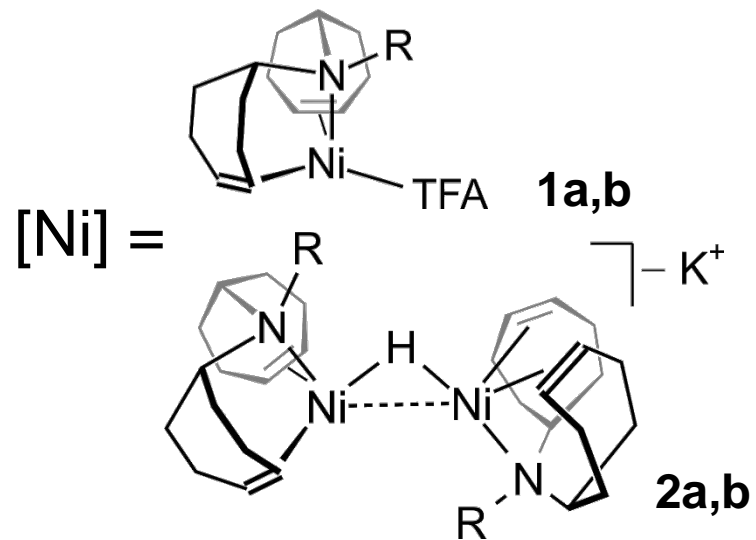
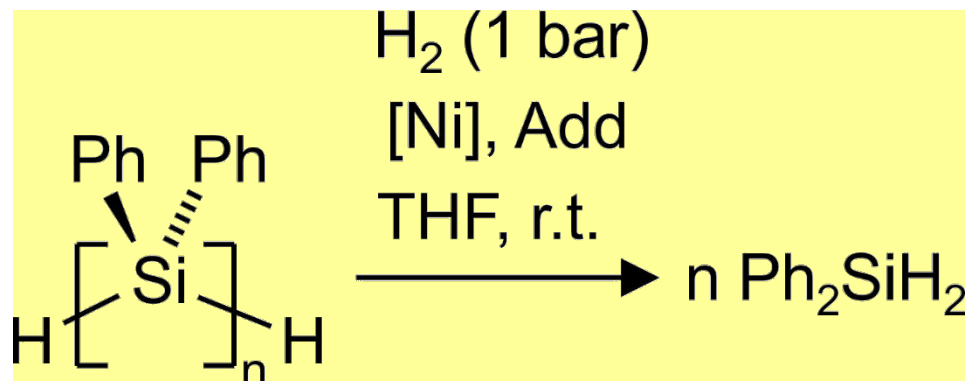
Ni-N	Ni-Si	C=C
2.23	2.25	1.43

$\delta \text{ } ^1\text{H} = 4.94 \text{ ppm}$
 $\delta \text{ } ^{29}\text{Si} = 18.5 \text{ ppm}$



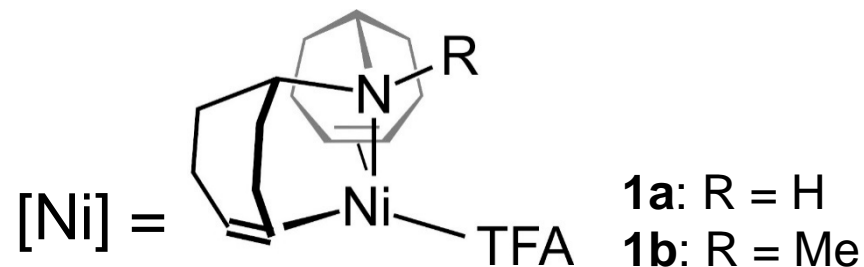
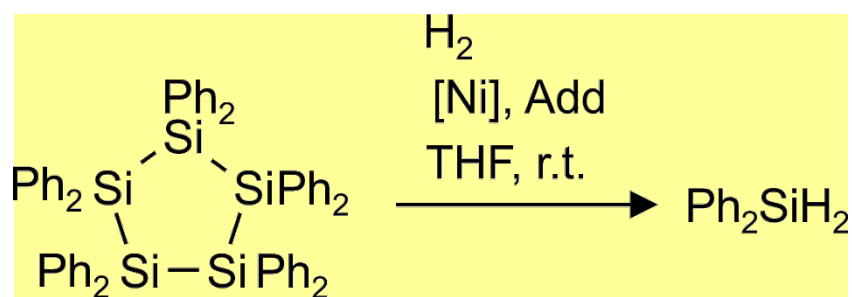
Cat.	Cat. [mol%]	Add (eqv.)	Conv. [%] (dimer : trimer : tetramer)
1a[a]	5	KAB (0.15)	NR
1a	5	KAB (0.15)	82 (2 : 1 : 0)
1b	5	KAB (0.15)	89 (1 : 4 : 0)
2a	1	-	80 (2 : 7 : 1)
2b	1	-	86 (11 : 14 : 1)
3	1	-	97 (0 : 2 : 1)
4a	1	-	80 (1 : 2 : 1)
4b	1	-	86 (1 : 2.5 : 0.7)

Reaction conditions: Silane (0.5 mmol) in THF (5 mL), 1 - 5 mol% [Ni], KAB (15 mol%) at r.t. under Ar flow after 48h. [a] Reaction in closed vessel.



Cat.	Cat. [mol%]	Add (eqv.)	t[h]	Conv. [%]
1a	5	KAB (0.15)	18	58
1b	5	KAB (0.15)	18	>98
1a	1	KAB (0.03)	48	>98
2a	1	KAB (0.03)	48	>98
2b	1	KAB (0.03)	48	>98

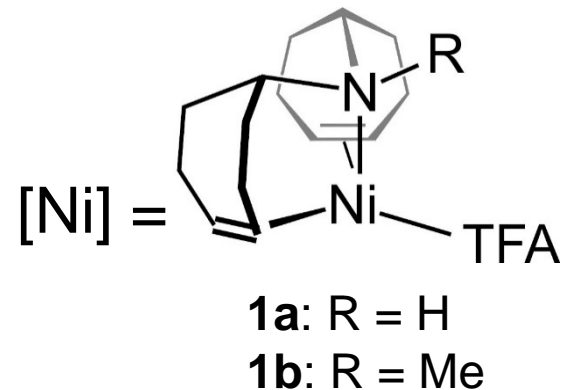
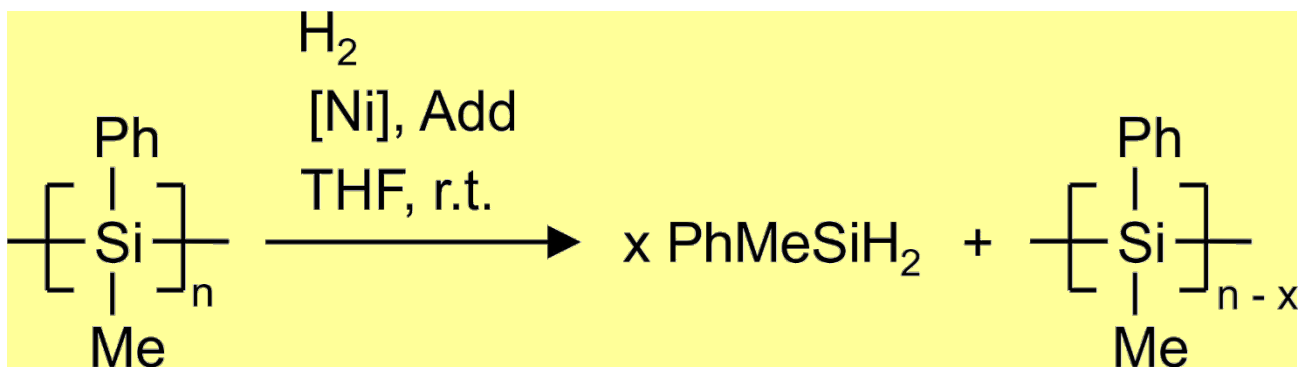
Reaction conditions: Silane (0.5 mmol) in 5 mL THF, 1 - 5 mol% [Ni], KAB (3 - 15 mol%) at r.t. under H₂ (1 bar).



Cat.	Cat.[mol%]	Add (eqv.)	H ₂ (bar)	t[h]	Yield [%] (monomer:dimer:trimer:tetramer)
1a	20	Li (2)	1	24	86 (20 : 1 : 2 : 1)
1b	20	Li (2)	1	24	91 (5 : 1.5 : 1 : 1)
1a	5	KOtBu (0.2)	1	48	85 (1 : 1.5 : 2.5 : 1)
1b	3	KOtBu (0.15)	3	48	64(50 : 1.5 : 0.5 : 1)
1b	1.5	KOtBu (0.15)	3	48	71 (8 : 1 : 0 : 0)
1b	3	KOtBu (0.15)	5	48	81 (40 : 1 : 0 : 0)

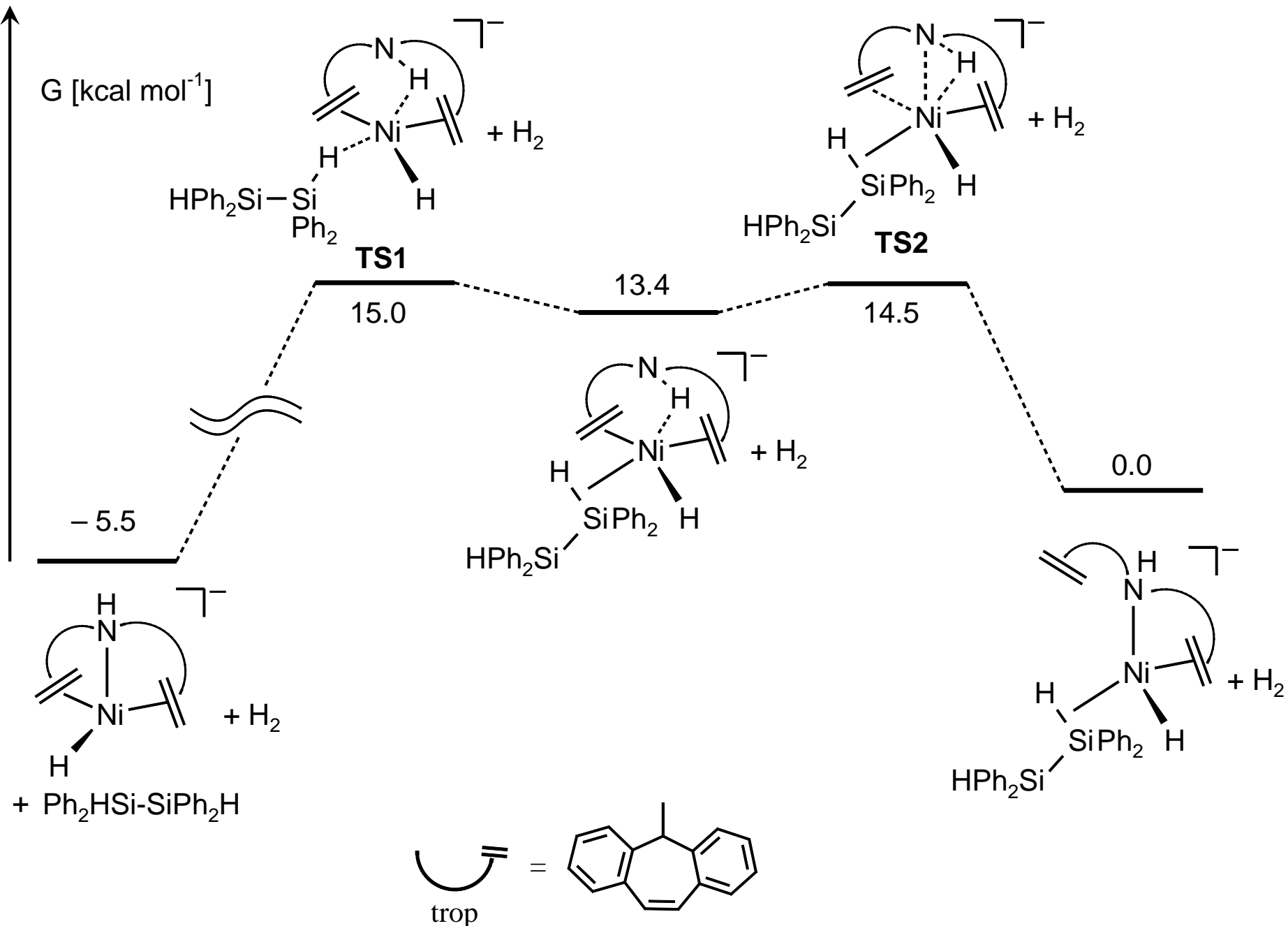
No reaction under H₂ pressure > 5 bar!

Reaction conditions: Silane (0.11 mmol) in THF (5 mL),
 1.5 - 20 mol% [Ni], additive at r.t. under H₂ (1 - 50 bar).



Cat.	Add (eqv.)	H ₂ (bar)	t[h]	Yield [%]
1b	KOtBu(0.1)	1	24	57
1b	Na (1)	1	48	42
1b	LiAlH ₄ (0.1)	1	24	64
1b	LiAlH ₄ (0.3)	1	38	60
1a	LiAlH ₄ (0.1)	5	18	61
1b	LiAlH ₄ (0.1)	5	18	79

Reaction conditions: Polysilane (0.5 mmol PhMeSi unit) in THF (5 mL), 1 mol% [Ni], additive at r.t. under H₂ (1 - 5 bar).



Gibb's energies
in kcal mol⁻¹

