Wacker-Lehrstuhl für Makromolekulare Chemie & Katalyse
Institut für Siliciumchemie

Bernhard Rieger

Technische Universität München

Kunststoffe im 21. Jahrhundert

Kommt der Kohlenstoff aus CO_2 ?

Workshop „CO_2: Klimakiller oder Werkstoff der Zukunft“
Materials Valley e.V.
Merck KGaA, Darmstadt, 10.05.2012

Zentralinstitut für
Katalyseforschung
Catalysis Research Center

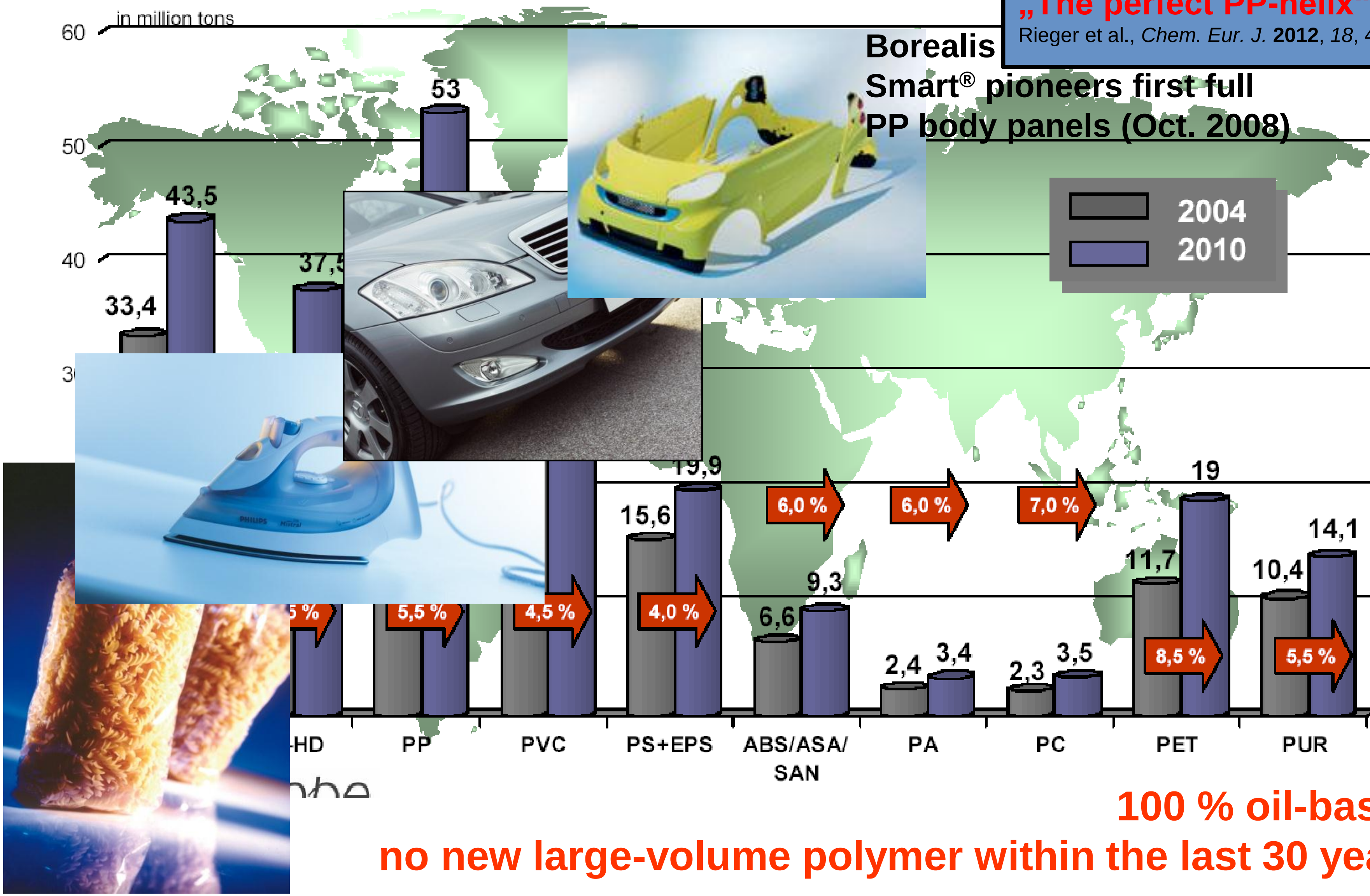
Deutschland
Land der Ideen
Ausgewählter Ort 2007

World Plastics Consumption 2004 - 2010

(Growth p.a.)

Ultra-rigid PP ?
„The perfect PP-helix“
Rieger et al., *Chem. Eur. J.* **2012**, *18*, 4174.

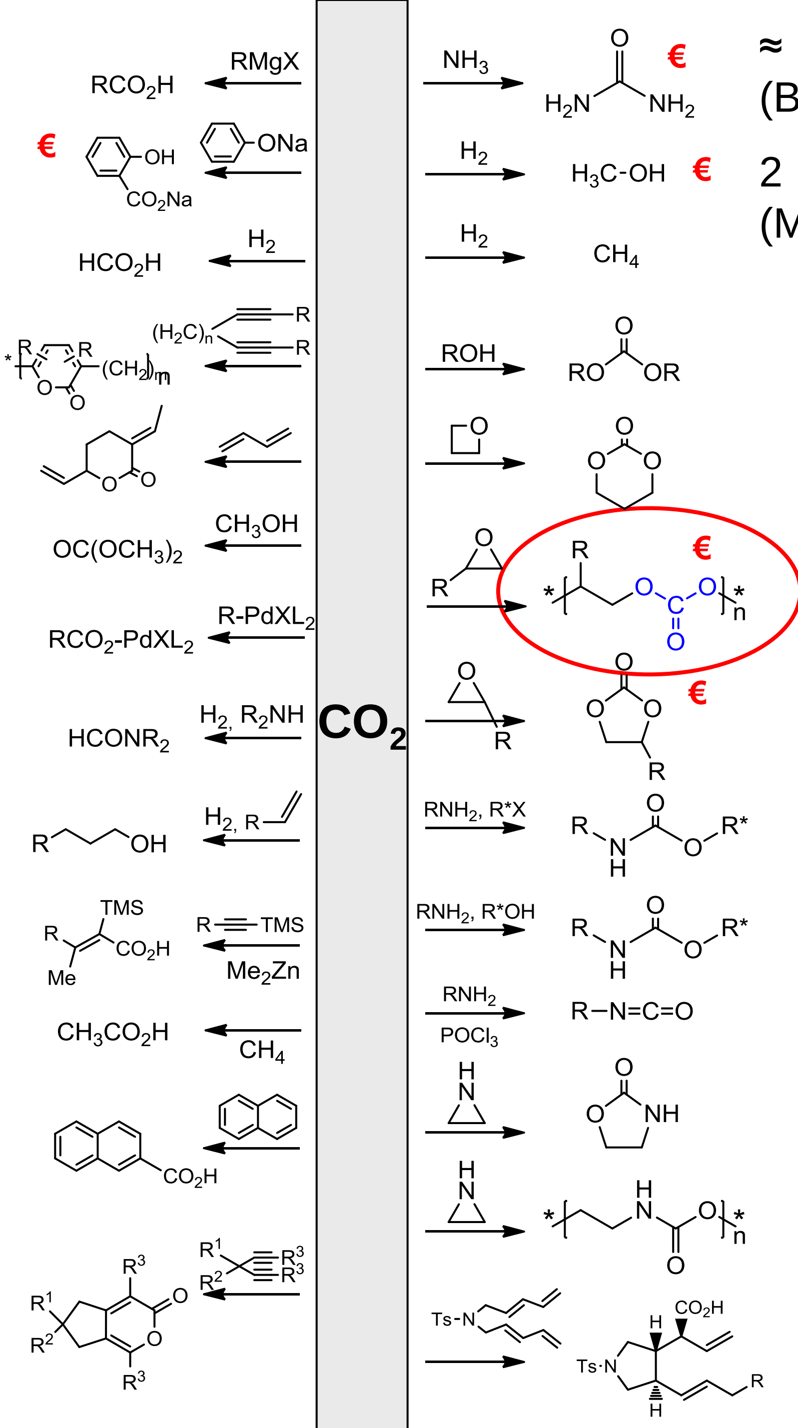
Borealis
Smart® pioneers first full PP body panels (Oct. 2008)



100 % oil-based
no new large-volume polymer within the last 30 years

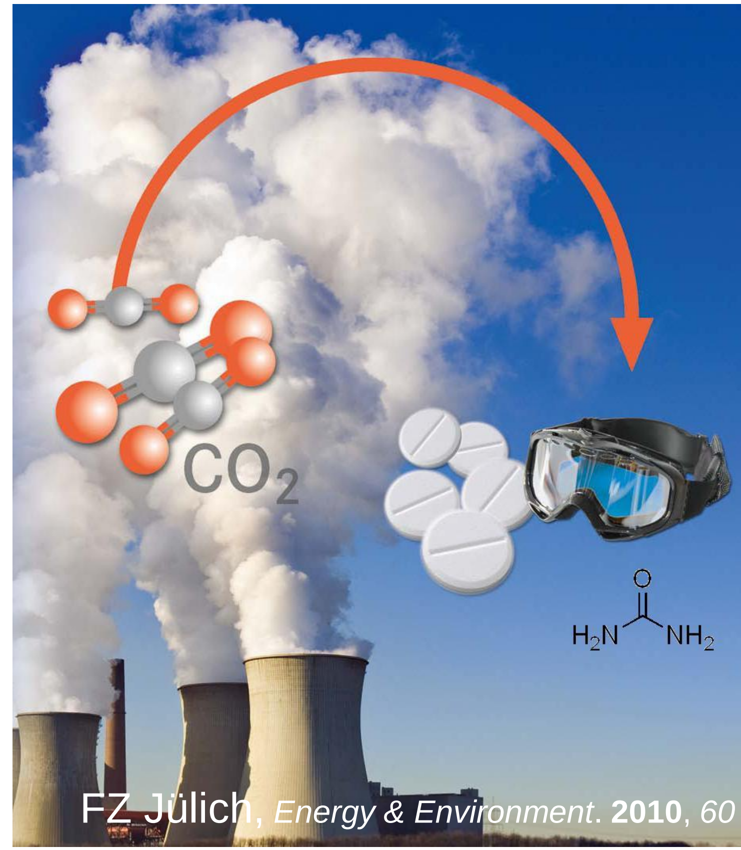
CO_2 Utilization „CCU“

(**C**arbon **C**apture & **U**tilization)



≈ 100 Mio t
(Bosch-Meiser 1922)

2 Mio t
(Mitsui 2008: \$12 Mio)



FZ Jülich, *Energy & Environment*. **2010**, *60*

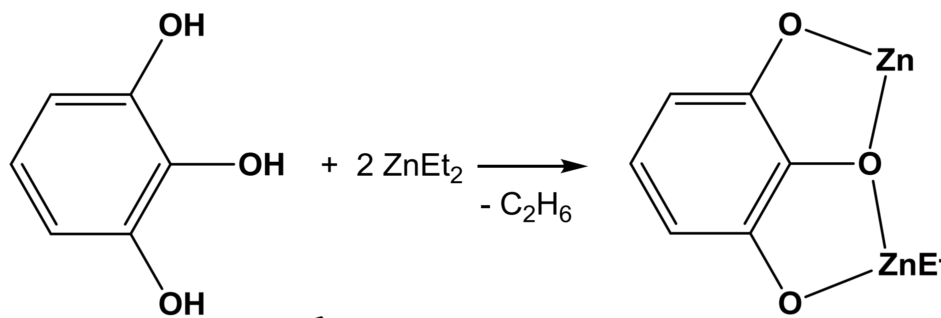
- Peters, Koehler, Kuckshinrichs, Leitner, Markewitz, Mueller, *Chemsuschem* **2011**, *4*, 1216
- Rieger, Herrmann, Kühn, *Angewandte Chemie*, **2011**, *123*, 8662
- Klaus, Lehenmeier, Anderson, Rieger *Coord. Chem. Rev.*, **2011**, 255, 1518

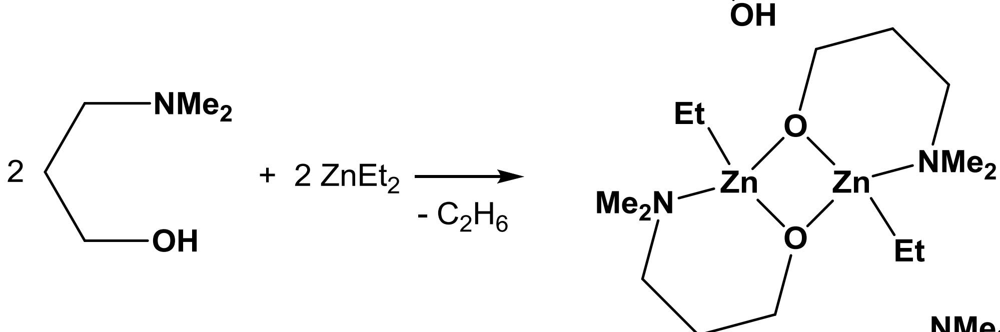
ali-Polycarbonates
The Start

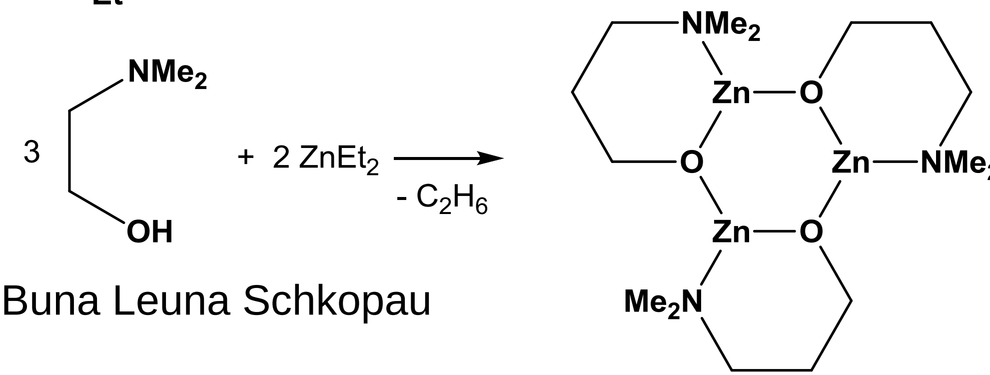
Inoue et al., *Makromol. Chem.* **1969**, *130*, 210
(JP 49031591, JP 48,068,695, Nippon Oil Company)

$$ZnEt_2 + H_2O \xrightarrow[- C_2H_6]{} \textbf{?}$$

Kuran et al., *Macromol. Chem.* **1981**, *C21*, 135



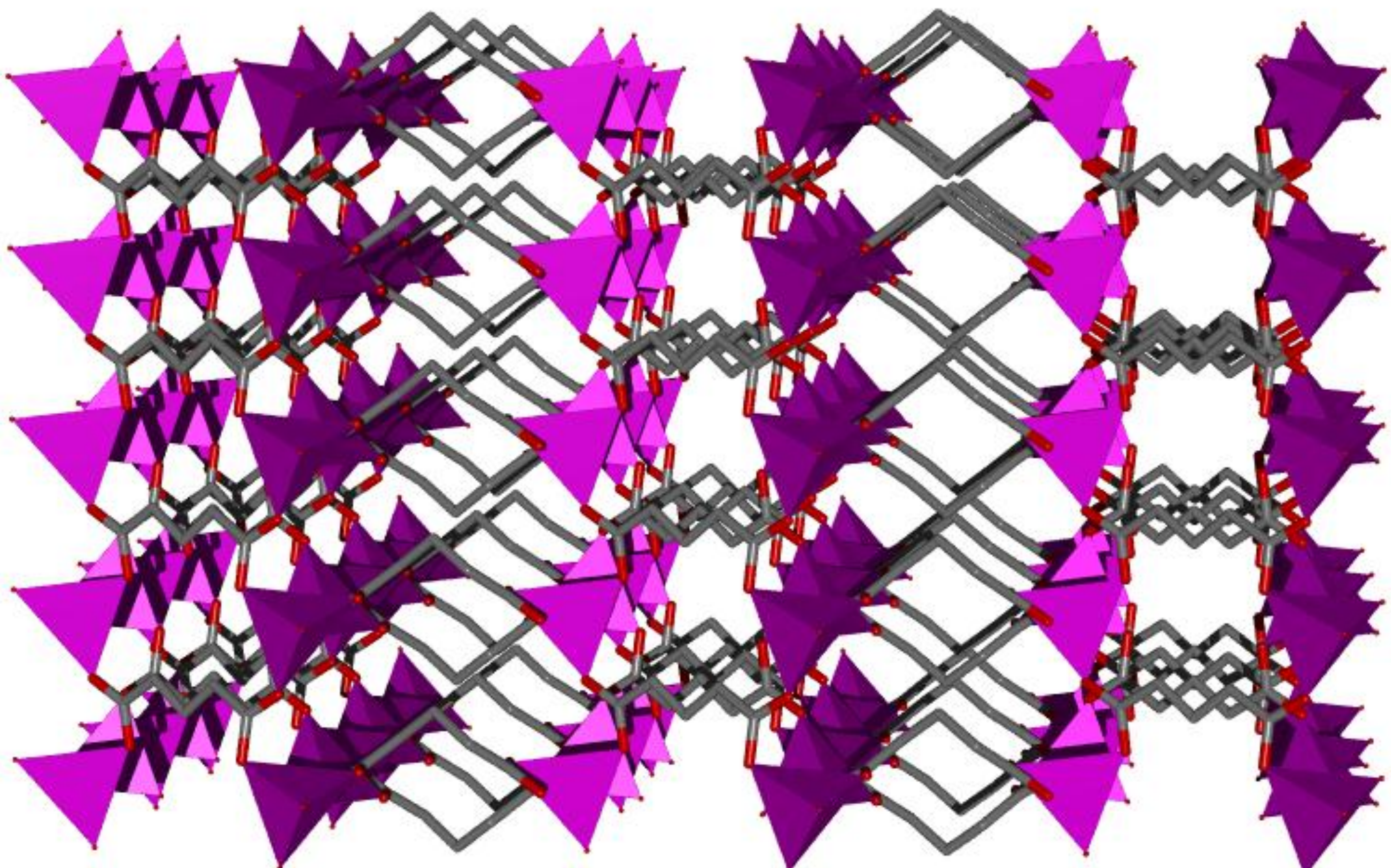




1970th - 90th: Mitsui, Arco, Air Products & Buna Leuna Schkopau

Soga … Zn-Glutarate (ZnO + glutaric acid)

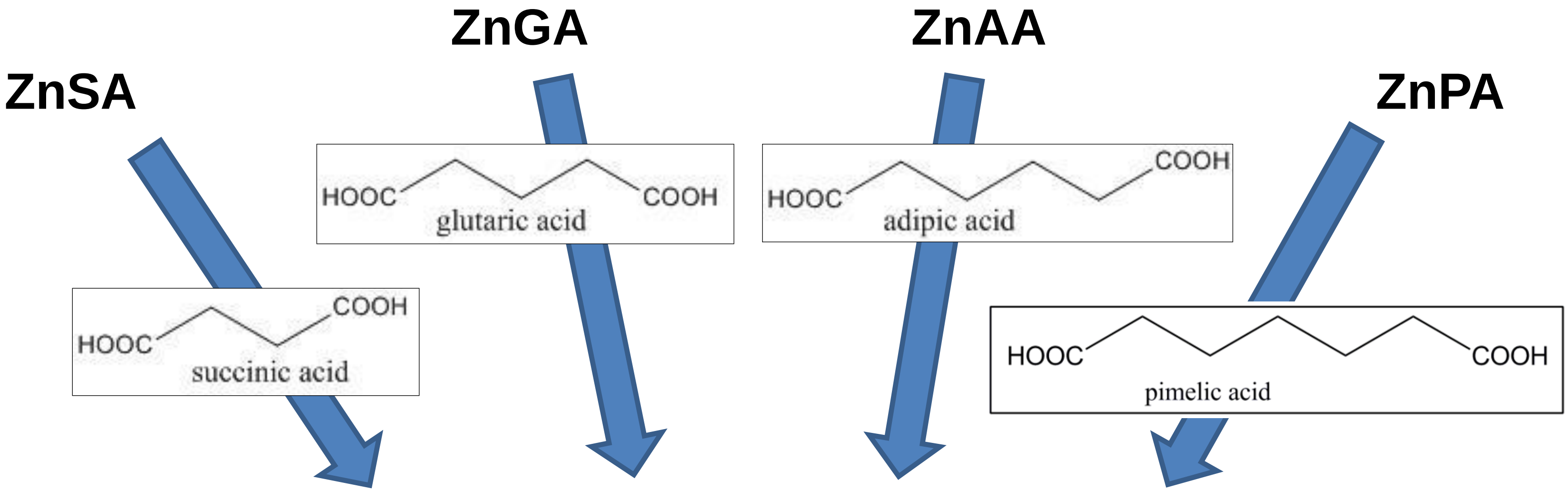
Soga et al *Polym. J.* **1981**, *13*, 407.
Rokicki, A.; Air Products and Chemicals, Inc.; Arco Chemicals Co. U.S. Patent 4,943,677, 1990, U.S. Patent 5,026,676, 1991. www.empowermaterials.com, DSM (Novomer 2010)



monoclinic, $P_{2/c}$

M. Ree et al., *Catal. Today,* **2006**, 115,134–145. (Zheng et al., *Z. Kristallogr.,* **2000**, *215*, 535.)

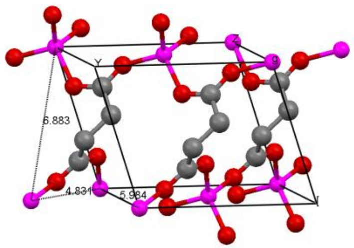
Zn(II) Precipitation Catalysts



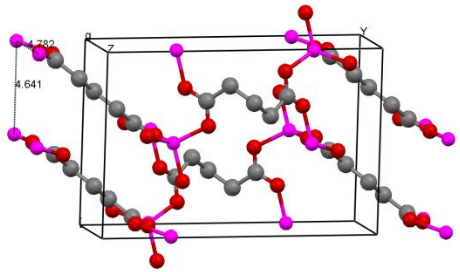
Catalyst	ZnSA	ZnGA*	ZnAA**	ZnPA***
Dicarboxylic acid	Succinic acid	Glutaric acid	Adipic acid	Pimelic acid
g poly /g cat	3	160	110	95
g poly.Zn $mol^{-1}.h^{-1}$	0.3	780	580	530

* Y. Z. Meng, *Polym. Sci. Part A Polym. Chem.*, **2002**, 40, 3579; ** J. T. Wang, *J. Appl. Polym. Sci.*, **2006**, 99, 200; *** Q. Zhu, *Polym. Int.*, **2003**, 52, 799

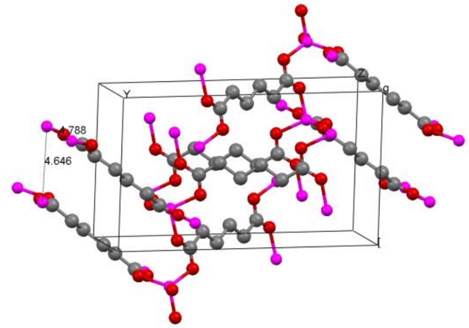
Zinc Dicarboxylates – Sold State Structure / Activity



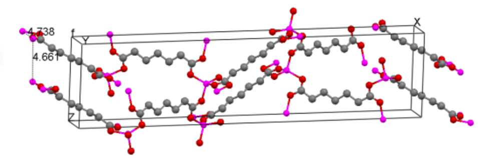
Zn-Succinate



Zn-Glutarate



Zn-Adipate



Zn-Pimelate

hkl	d_{Zn-Zn}	d_{Zn-Zn}
100	/	/
010	/	/
001	4,83	/

g/g ZnGA	3
$g \cdot mol^{-1} \cdot h^{-1}$	0.3

hkl	d_{Zn-Zn}	d_{Zn-Zn}
100	4.64	4,78
010	4.64	/
001	4,78	/

g/g ZnGA	160
$g \cdot mol^{-1} \cdot h^{-1}$	780

hkl	d_{Zn-Zn}	d_{Zn-Zn}
100	4.64	4,78
010	4,64	/
001	4,78	/

g/g ZnGA	110
$g \cdot mol^{-1} \cdot h^{-1}$	580

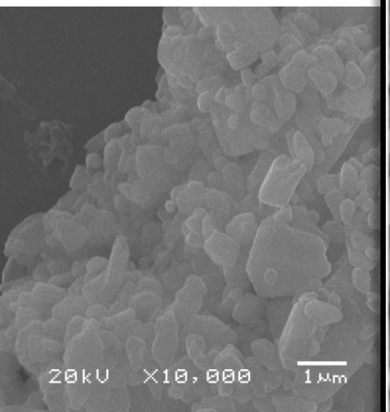
hkl	d_{Zn-Zn}	d_{Zn-Zn}
100	4.66	4.74
010	4.66	/
001	4,74	/

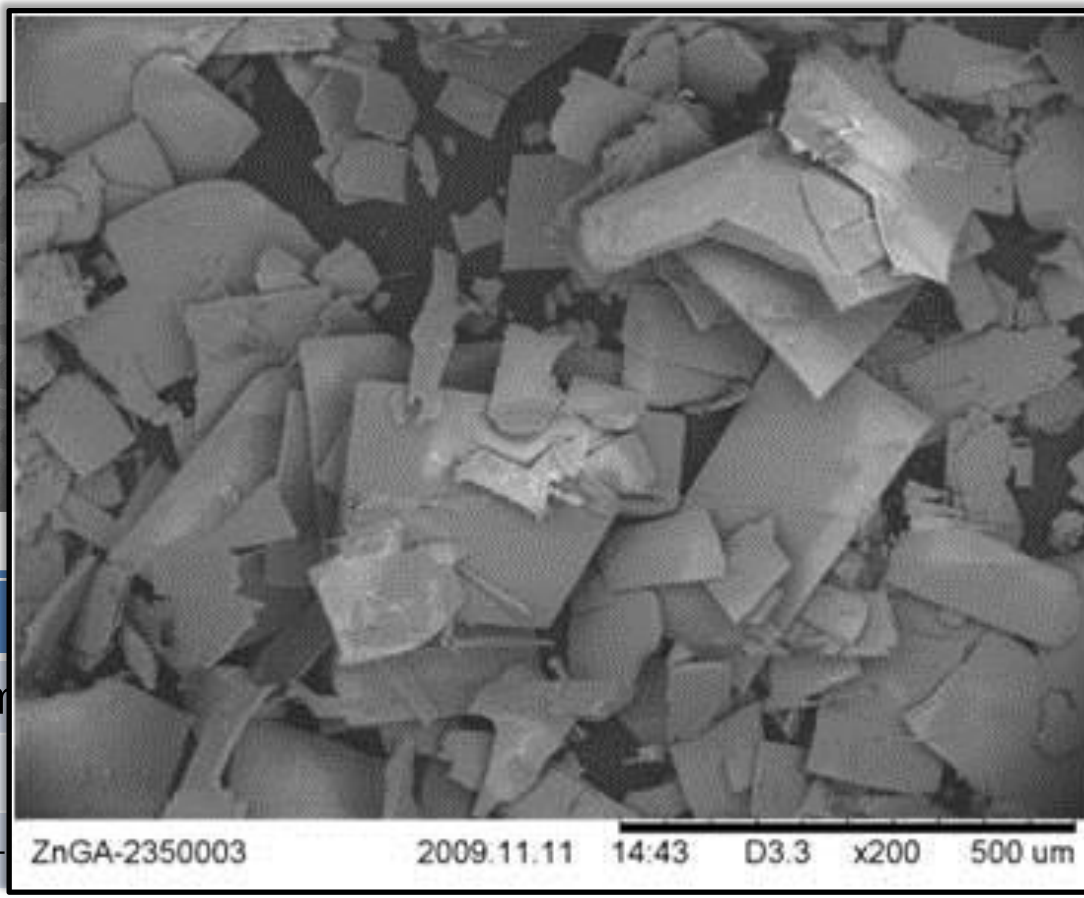
g/g ZnGA	95
$g \cdot mol^{-1} \cdot h^{-1}$	530

S. Klaus, M. W. Lehenmeier, E. Herdtweck, P. Deglmann, A. K. Ott, B. Rieger, ***J. Am. Chem. Soc.***, **2011**, *133*, 13151

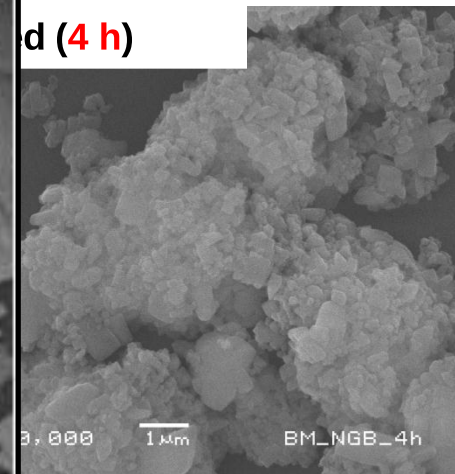
Ball-Milling – A Concept for Activity Increase ?

ball-milled (30 min)





d (4 h)

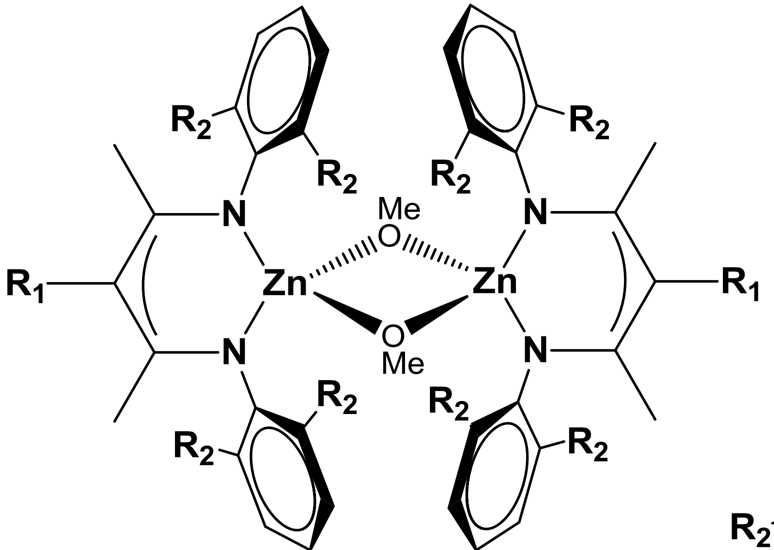


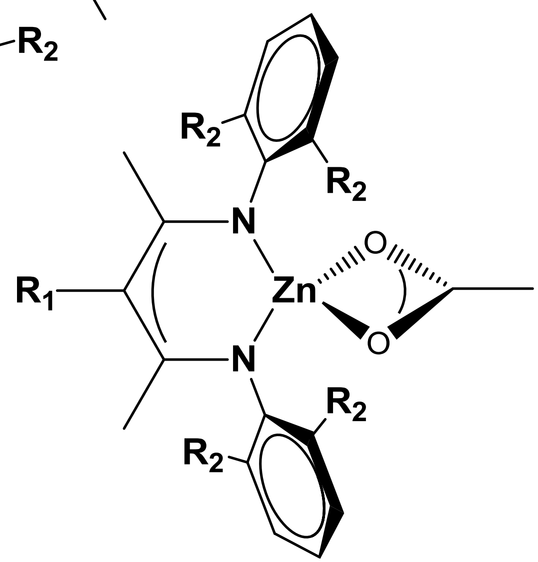
Catalyst	A	ZnGA
ball-milling (m		240
g/g cat		70
$g \cdot mol^{-1} \cdot h^{-1}$	)	680

ball-milling in inert condition → no activity

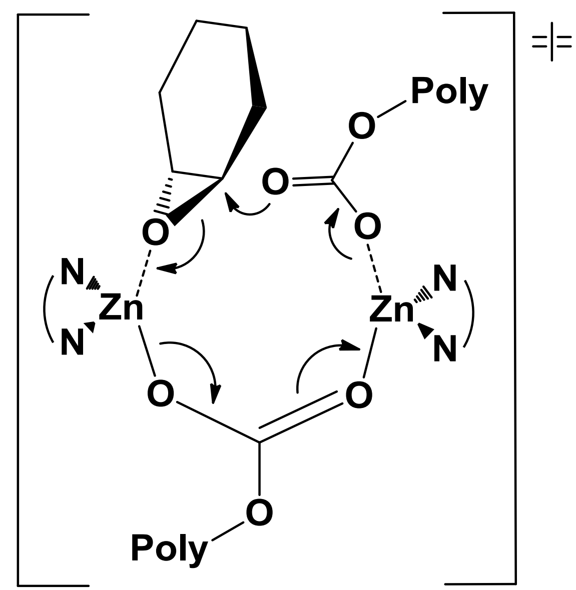
activation with H_2O necessary → formation of initiator groups

Zn(II) β-Diketiminato Complexes
Rapid **CHO**-Polymerization



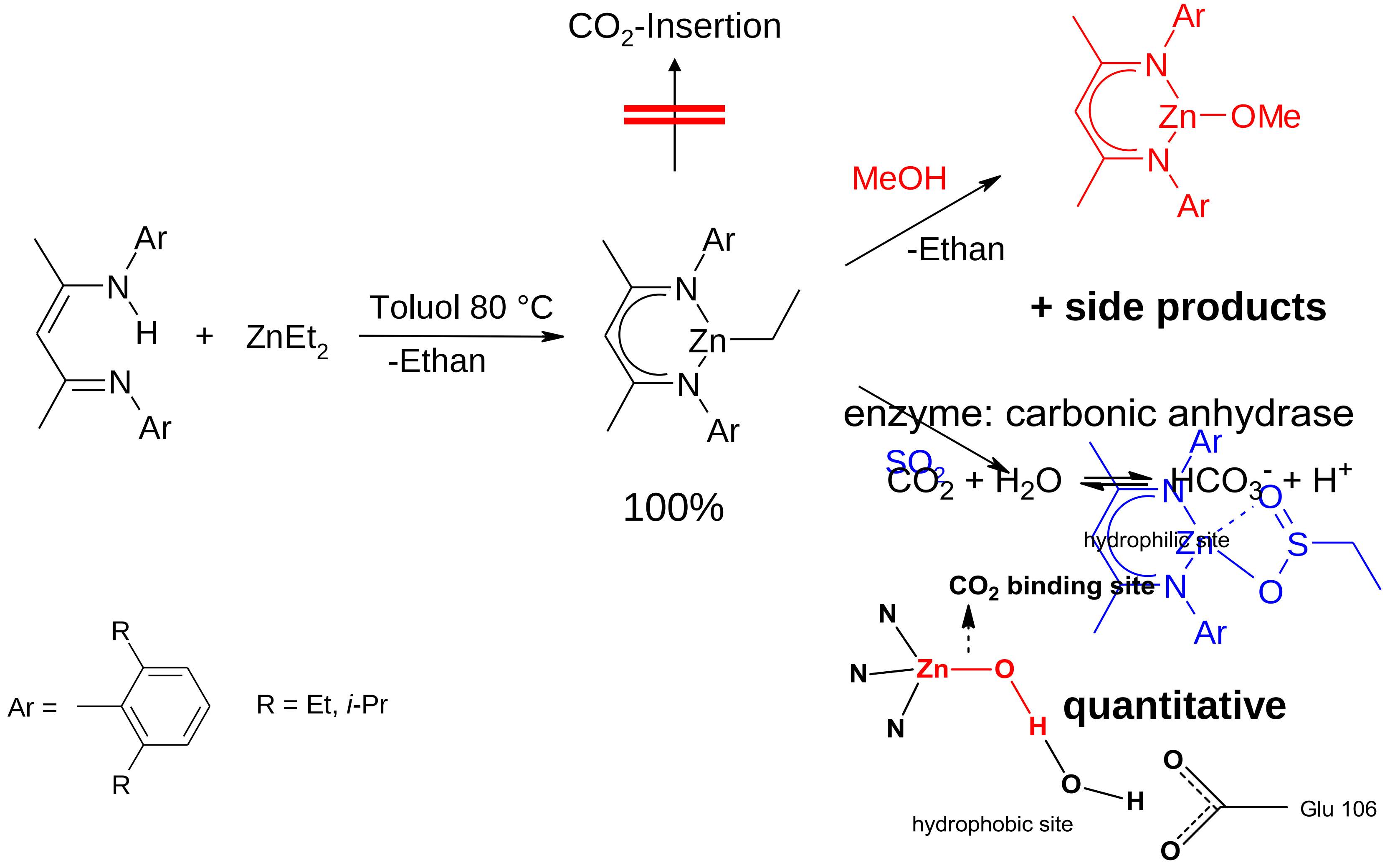


Bimetallic Mechanism ?



Coates et al,. *J. Am. Chem. Soc.* **1998**, *120*, 11018; Coates et al. *J. Am. Chem. Soc.* **2002**, *124*, 14284;Coates et al. *J. Am. Chem. Soc.* **2003**, *125*, 11911; Coates et. al., *Angew. Chem., Int. Ed.* **2004**, *43*, 6618

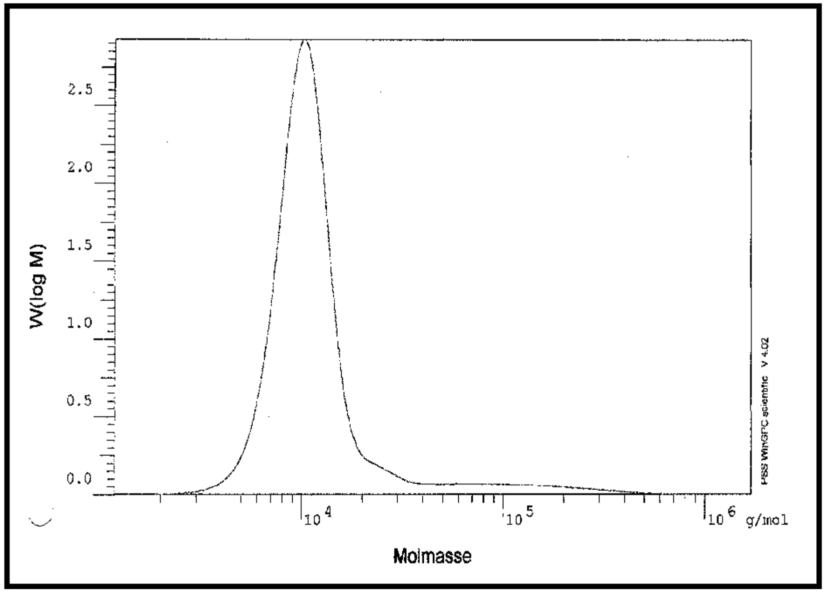
Single Component Catalysts (SCC)



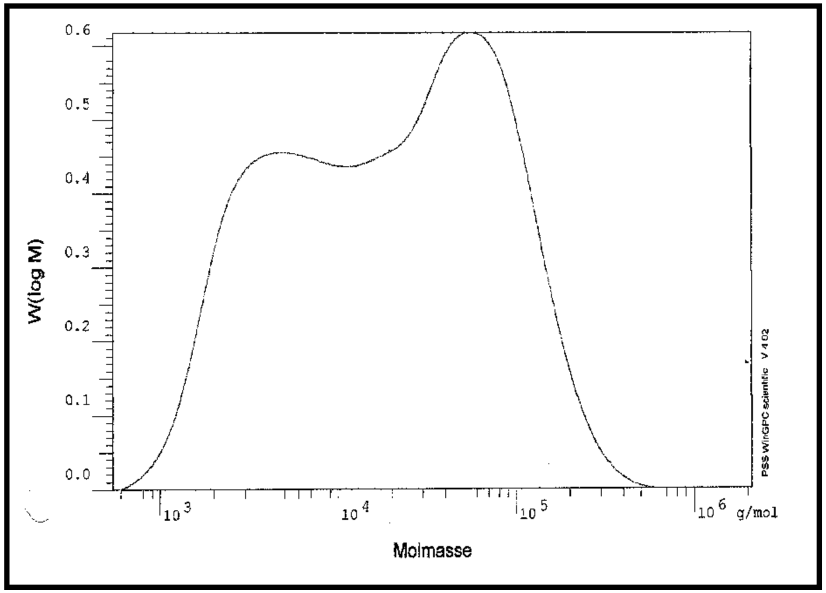
Eberhardt, Allmendinger, Luinstra, Rieger, *Organometallics* **2003**, *22(1), 211*

Poly(Carbonate)
Molecular Weight Distribution

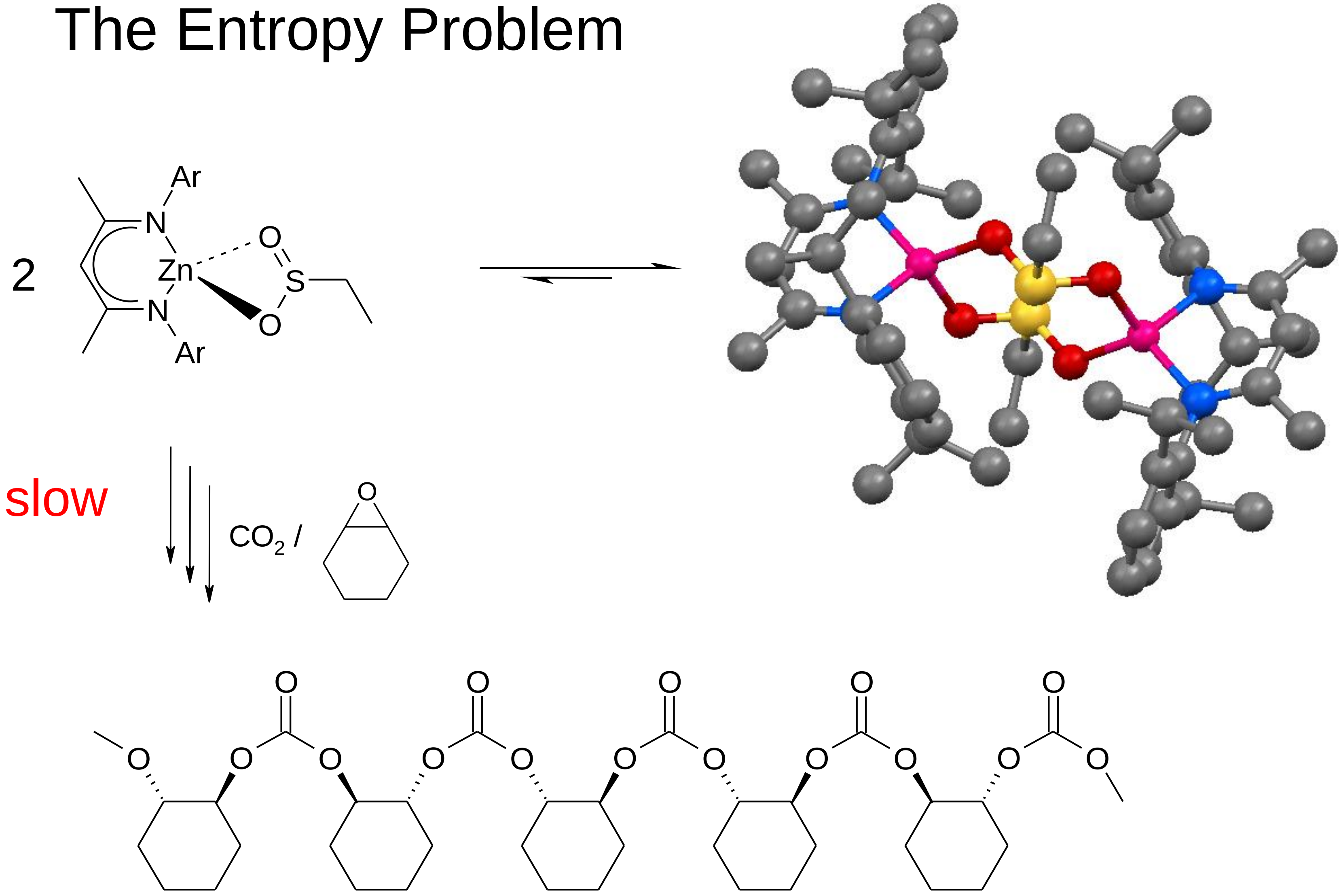
120 min / 60°C

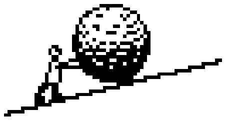


20 min / 60°C



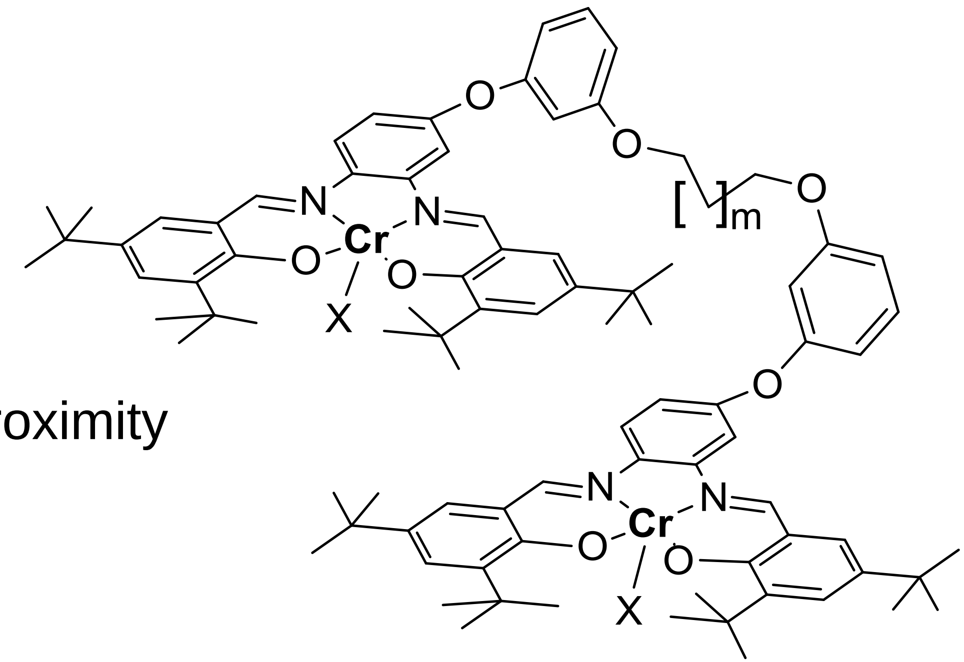
Two Active Sites - The Entropy Problem





Flexible Tethers – Bifunctional Catalysis

„Tethered“ Bimetallic systems

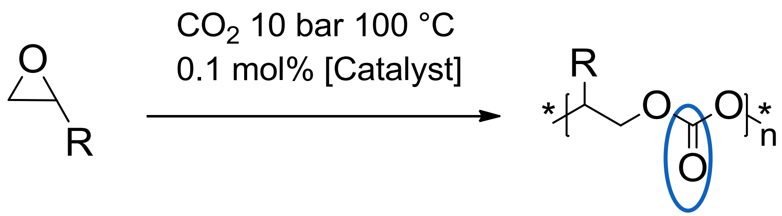


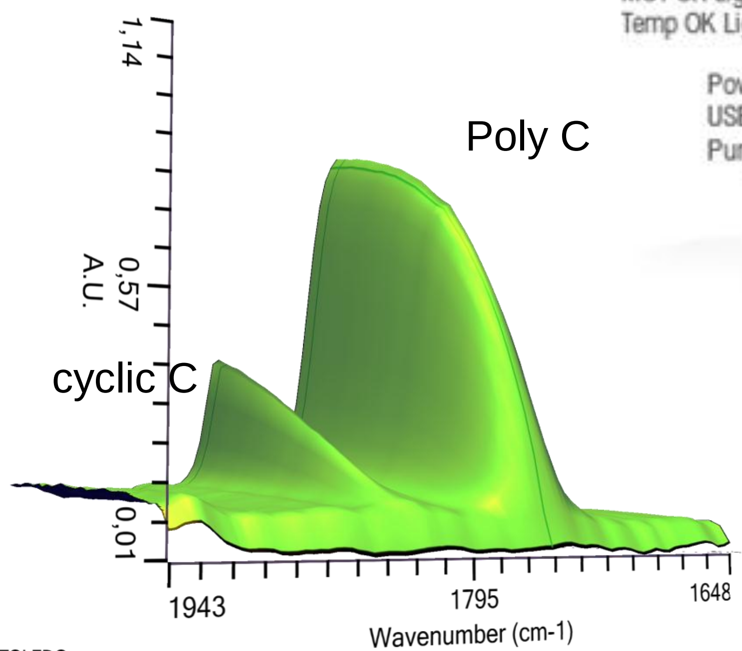
- Metal sites held in close spatial proximity
- Conformationally flexible tether

Mono-nuclear Cr(III)-Salen Complexes: Darensbourgh et al. *J. Am. Chem. Soc*., **1999**, *121*, 107
Darensbrough et al. *Coord. Chem. Rev.* **2007**, *107*, 2388

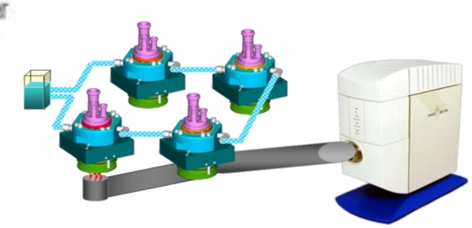
Di-nuclearity: Luinstra, Haas, Molnar, Bernhart, Eberhardt, Rieger, *Chem. Eur. J.* **2005**, 11, 6298
S. I. Vagin, R. Reichardt, S. Klaus, B. Rieger, *J. Am. Chem. Soc.* **2010**, *132*, 14367-14369
S. Klaus, M. W. Lehenmeier, C. E. Anderson, B. Rieger, *Coord. Chem. Rev.* **2010**, 255, 1518

CO_2 Copolymerization Kinetics

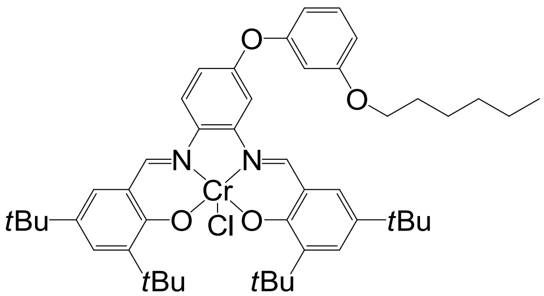


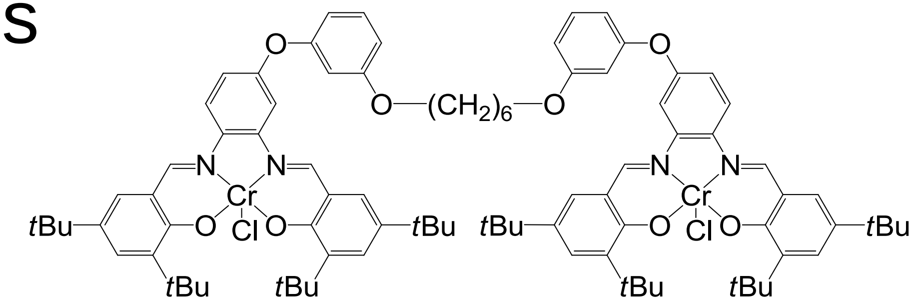


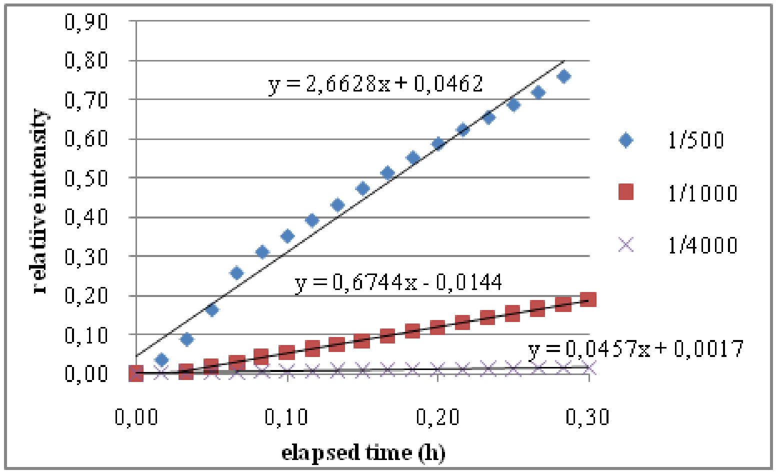
METTLER TOLEDO



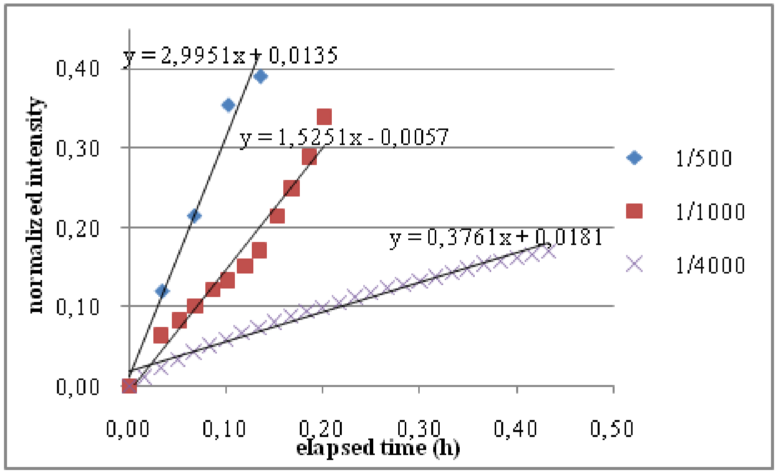
Kinetics

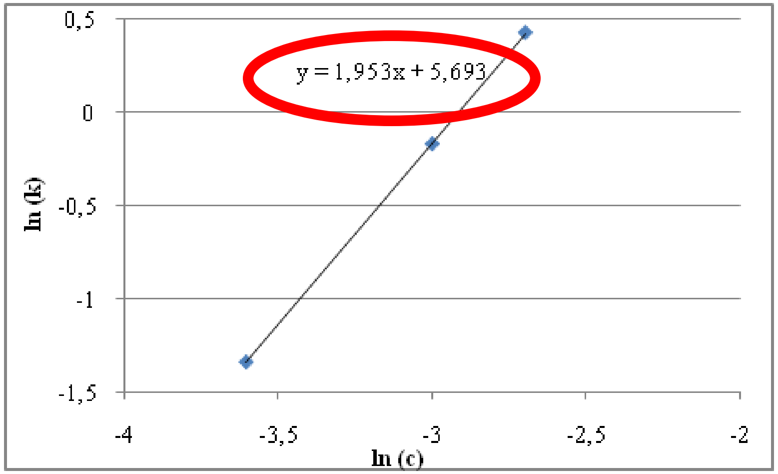




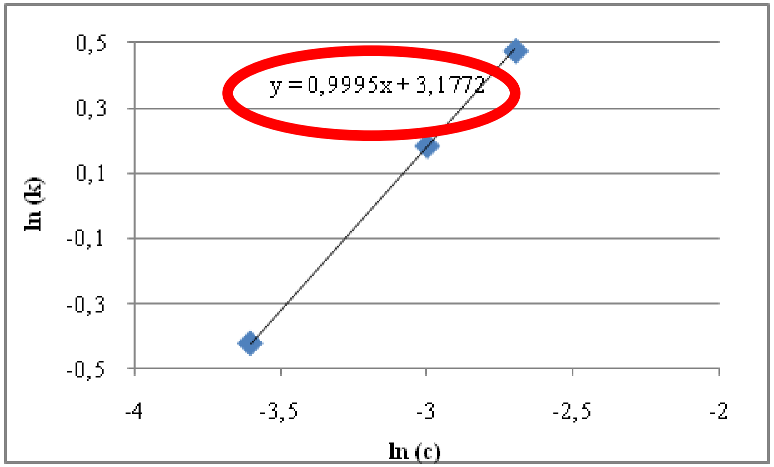


Initial rates of PPC synthesis catalyzed at different Cr/PO concentrations (1/500, 1/1000 and 1/4000).



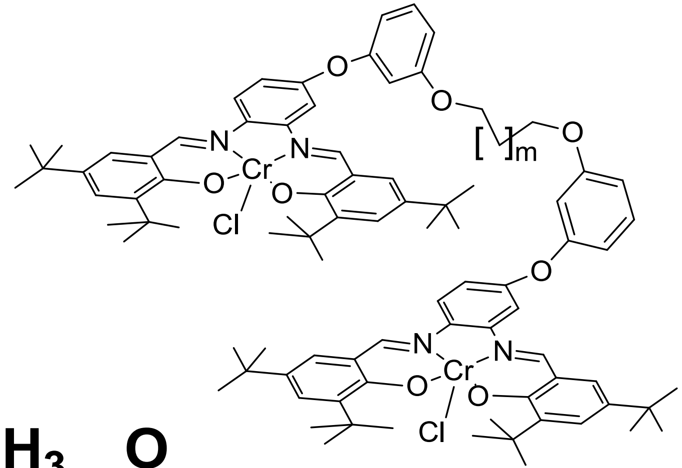


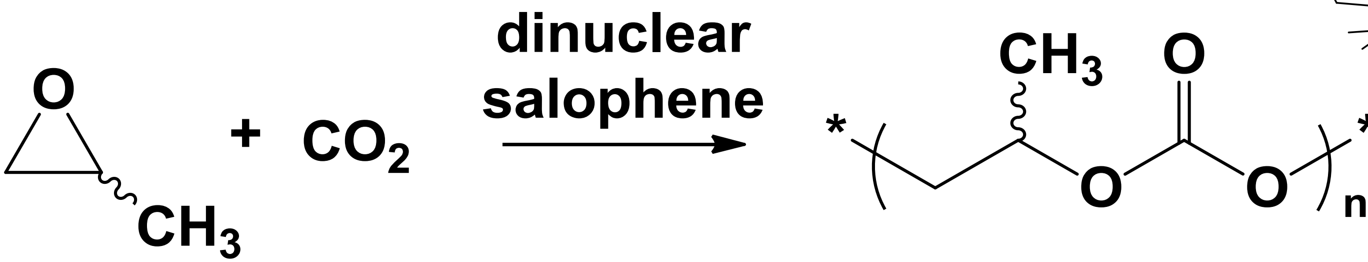
Plot of $\ln(k_{obs'})$ against $\ln([\textit{catalyst}])$.



Cooperative Effects

not optimized yet





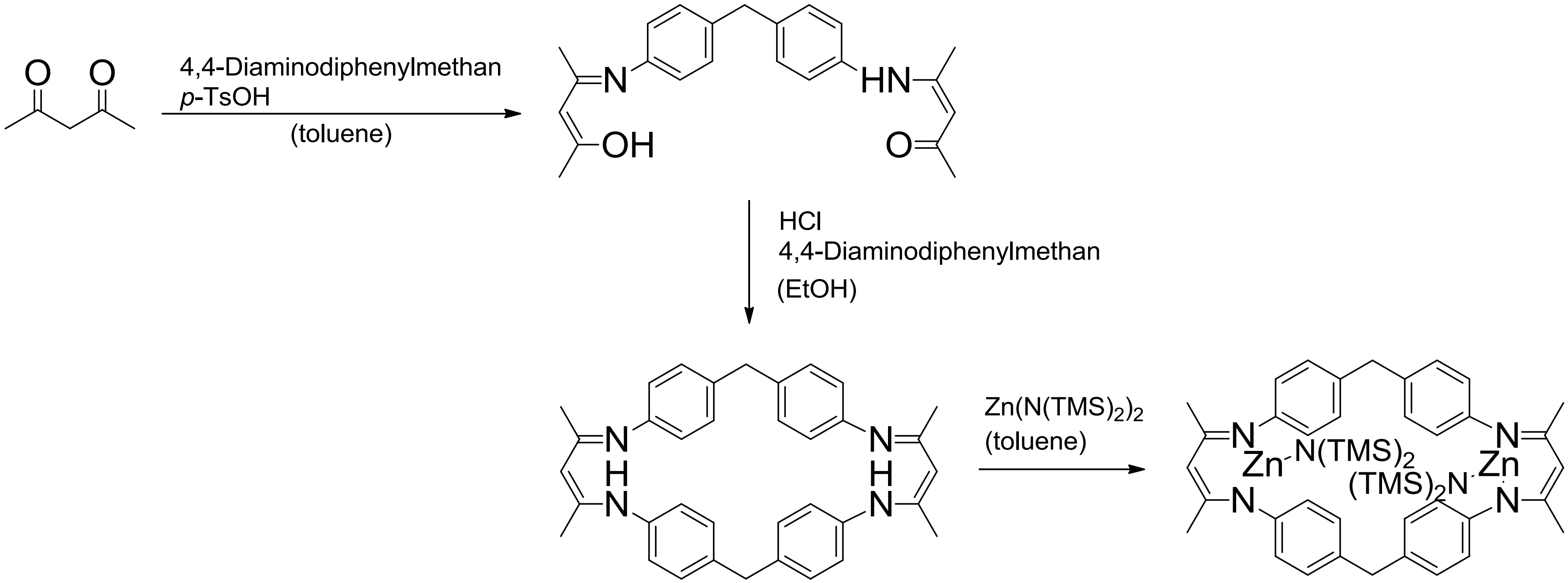
Catalyst	[PO]/[Cr]	PO/CO_2	cycl. C /%	TOF	M_w	PD
m = 4	2,000	2.3	0	49	40,000	1.8
m = 4	20,000	2.4	< 2	82	46,000	3.3

too slow for continuous process

… and it is Chromium !

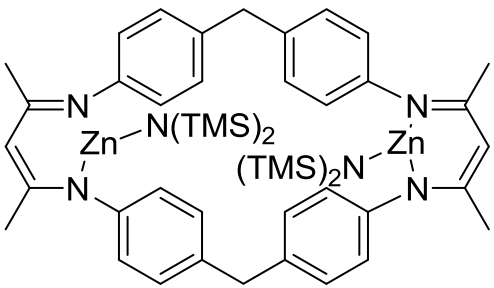
S. I. Vagin, R. Reichardt, S. Klaus, B. Rieger, *J. Am. Chem. Soc.* **2010**, *132*, 14367-14369

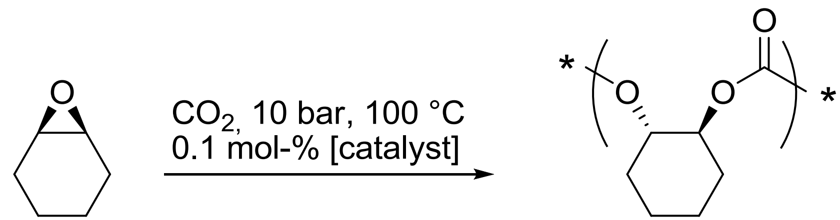
Stay With Zinc – Use Cooperative Effects



- 3-Step procedure
- High yields
- Kinetically stable complexes

Highest Activity Copolymerization





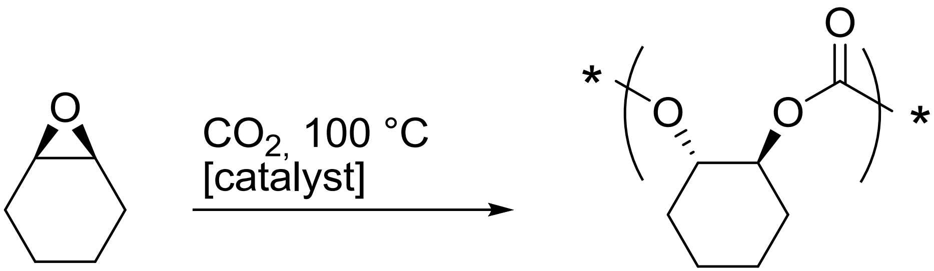
M_n: 45 kDa
PDI: 1.5

Promising:

- less than 1% cyclic carbonate
- TOF up to 7000 h^{-1} ([a] literature: 2860 h^{-1})

[a] T. Bok, H. Yun, B. Y. Lee, *Inorg. Chem.* **2006**, *45* , 4228

A Change in The Rate Law



- Coates[a] mono-nuclear complexes

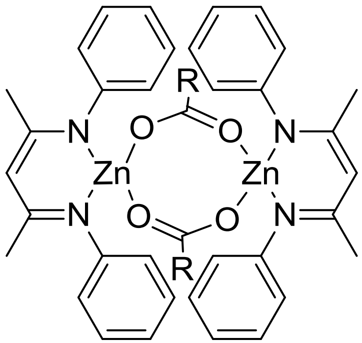
$$r = k \cdot [CHO]^{1} \cdot [CO_2]^{0} \cdot [Kat]^{1.7} \text{ for 10 bar } CO_2$$

- Di-nuclear catalyst

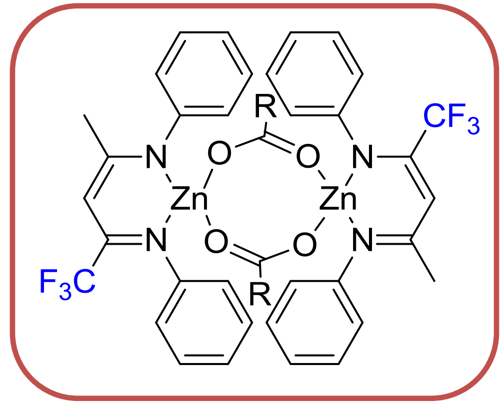
$$r = k \cdot [CHO]^{0} \cdot [CO_2]^{1} \cdot [Kat]^{1} \text{ for 5-25 bar } CO_2$$

M. W. Lehenmeier, C. Bruckmeier, S. Kissling, P. T. Altenbuchner, A.-K. Brym, B. Rieger, **2012**, submitted
Patent pending

A Solution For PO/CO_2 in a *Continuous* Process ?

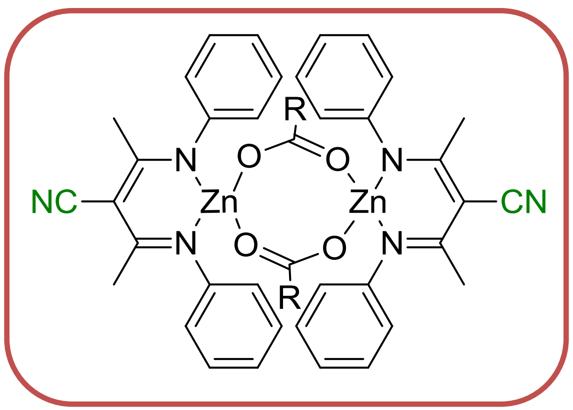


+ 41.6 kJ/mol

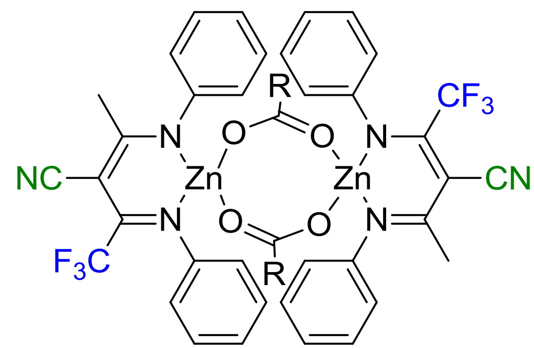


+ 65.1 kJ/mol

Work with PO



+75.1 kJ/mol



+106.9 kJ/mol

R: O-*i*Pr

Dr. Deglmann, BASF SE: Dissociation Energies

S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 14284

Monomers of Choice:
Propylene Oxide / CO_2

- **Elongation at Break ≈ 600%**
- **Tough**
- **Transparent**
- **Pleasant Haptics**
- **UV-Stable**
- **Biodegradable**
- **Processable (extrusion & injection molding)**

Molecular

- **High molecular weights 2×10^6 – 6×10^6 g mol^{-1}**
- **CO_2-content: 35 – 43 wt-%**
- **Carbonate linkage: 80 – 100 %**

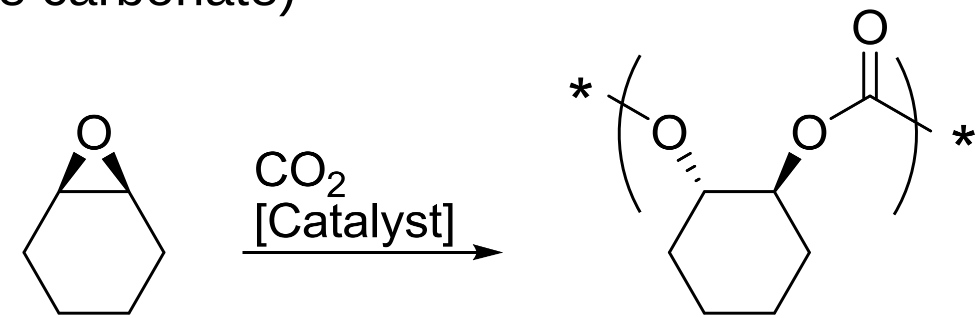
Thermal

- **TGA no decomposition up to 230°C**
- **T_m = none observed; T_g = 25 - 40°C**

G. A. Luinstra, *Polym. Rev.* **2007**, *48*, 192

Properties of PCHC

Poly(cyclohexene carbonate)

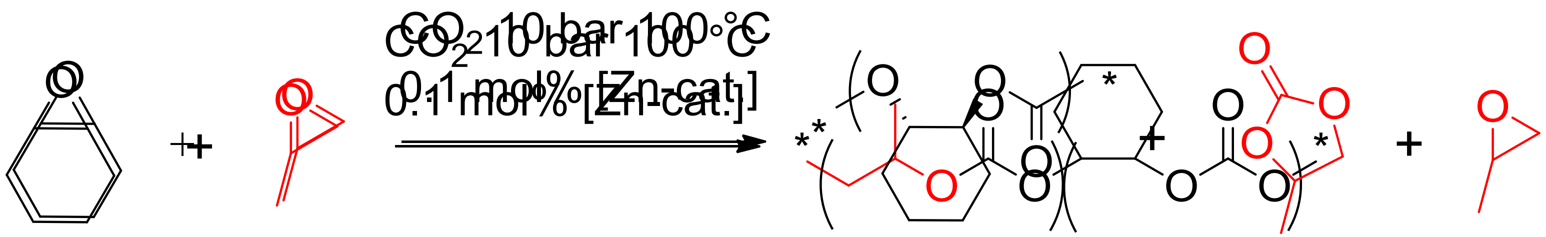


- brittle
- T_g up to 120 °C
- epoxide not available on large scale
- CO_2 content lower

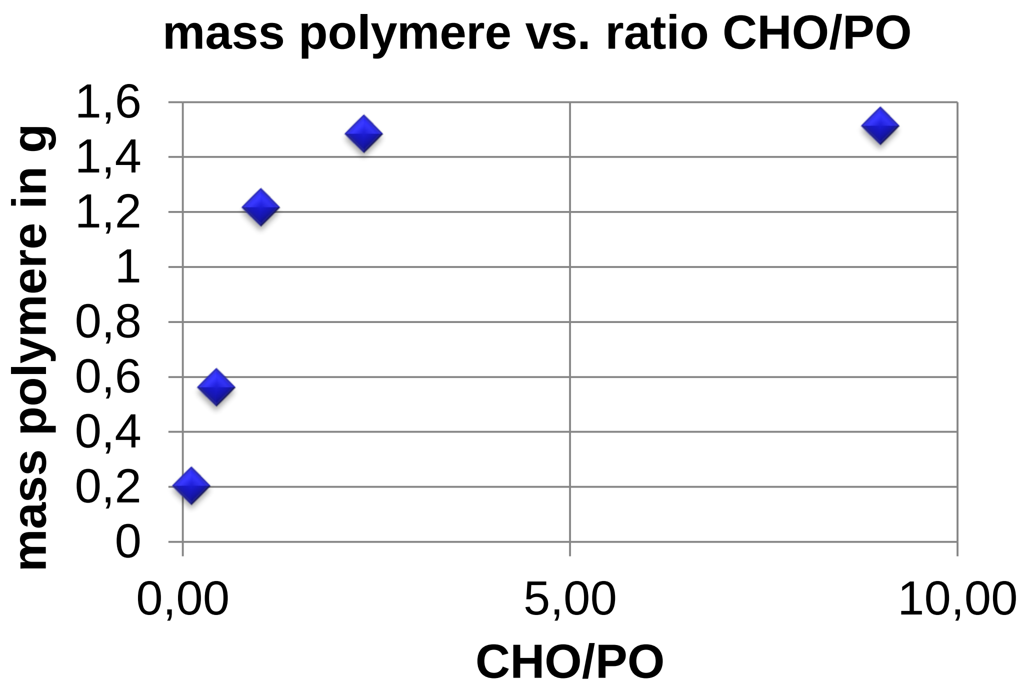
W.-M. Ren, X. Zhang, Y. Liu, J.-F. Li, H. Wang, X.-B. Lu, *Macromolecules* **2010**, *43*, 1396 – 1402

Terpolymerization (→ Tg Increase) with Zn(II)-based Catalysts

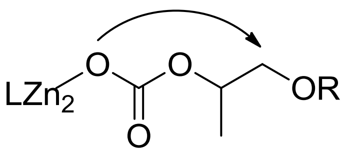
→ only poly(cyclohexene carbonate) formation

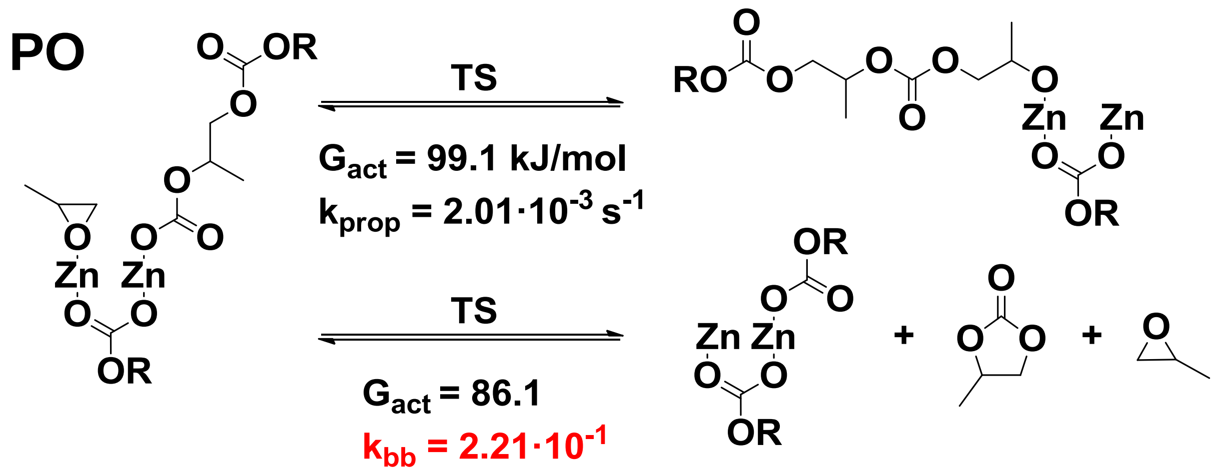


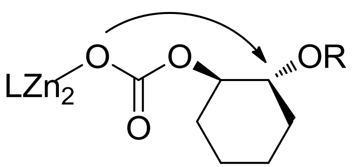
ratio CHO	/	PO
9	/	1
7	/	3
1	/	1
3	/	7
1	/	9

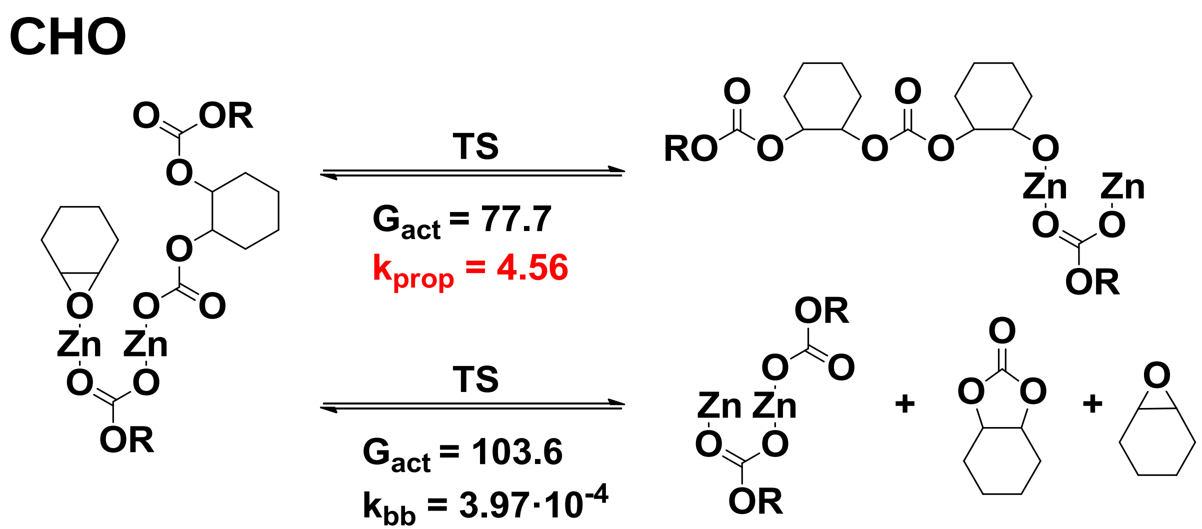


Reaction Rates – Propagation / Back-Biting (bb)







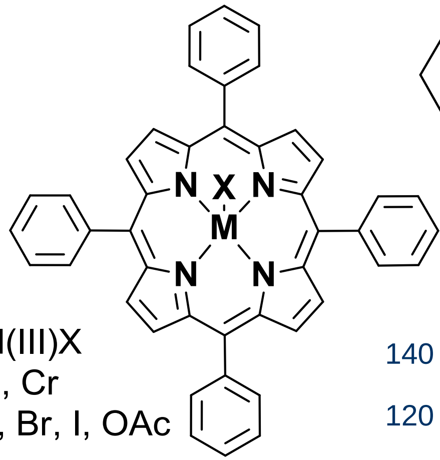


$v_{bb}(PO) \gg v_{bb}(CHO)$

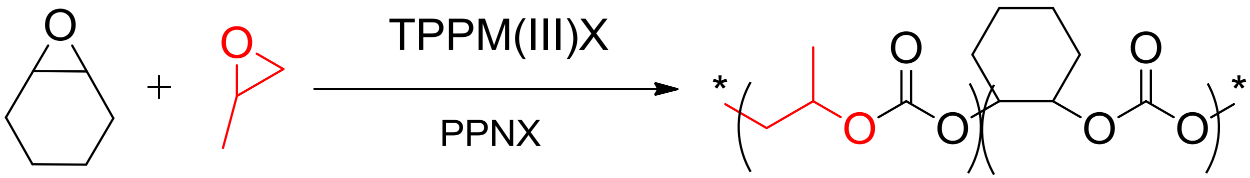
prop: propagation

Lehenmeier, Bruckmeier, Klaus, Dengler, Deglmann, Ott, Rieger, *Chem. Eur. J.* **2011**, *17*, 8858

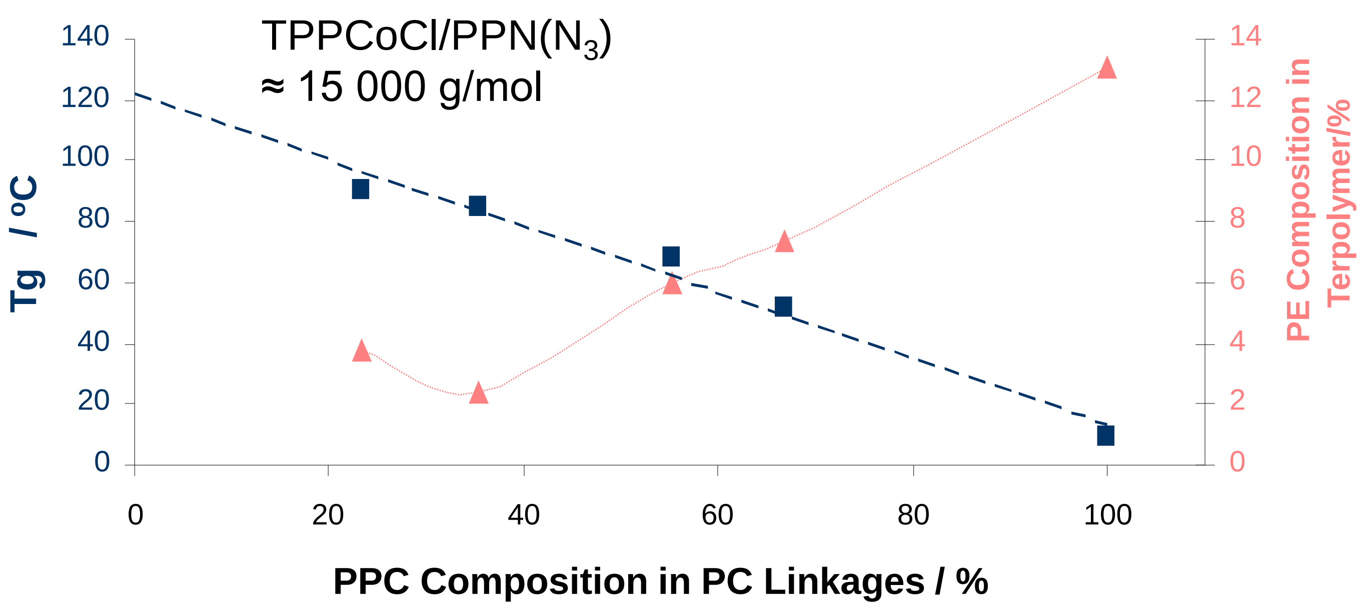
Porphyrins for Regioregular PPC



TPPM(III)X
M: Co, Cr
X = C, Br, I, OAc



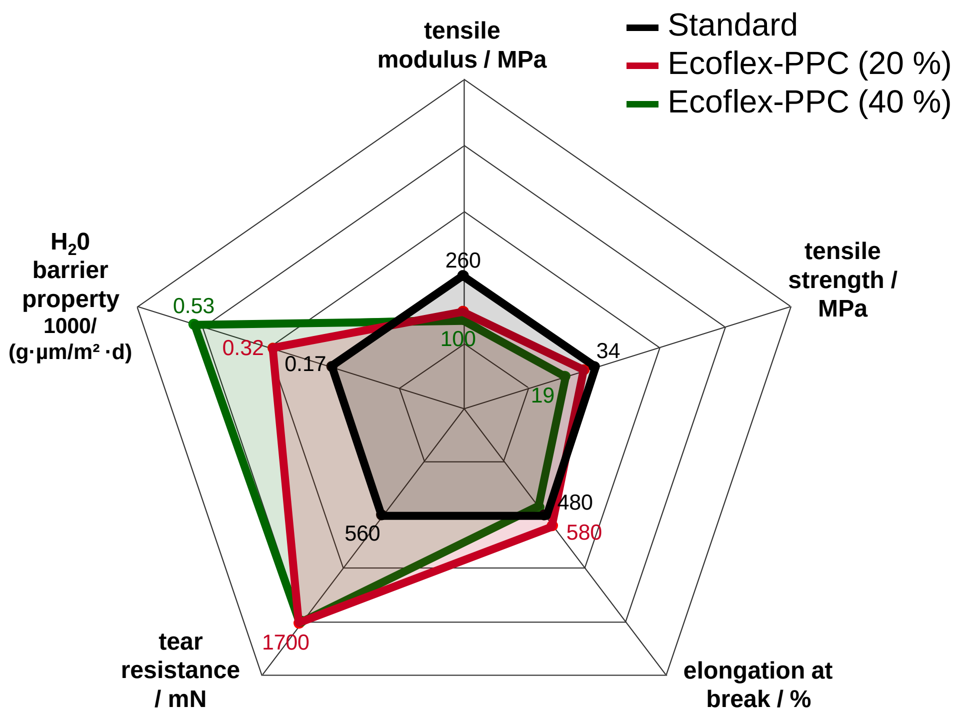
H-T > 90%



PPN: bis(triphenyl phosphin)iminium

J. Polym, Sci., Polym. Chem., 46, **2008**, 5959. MSc. Ivy Lim, Master Thesis, TUM, **2008** (with BASF SE)
L. Shi, X. Lu, R. Zhang, X. Peng, Ch. Zhang, J. Li, X. Peng, *Macromolecules* **2006,** *39,* 5679-5685
W. Ren, X. Zhang, Y. Liu, J. Li, H. Wang, X. Lu, Macromolecules **2010**, 43, 1396.

Blends



BMBF - Technologien für Nachhaltigkeit und Klimaschutz, Chemische Prozesse und stoffliche Nutzung von CO_2

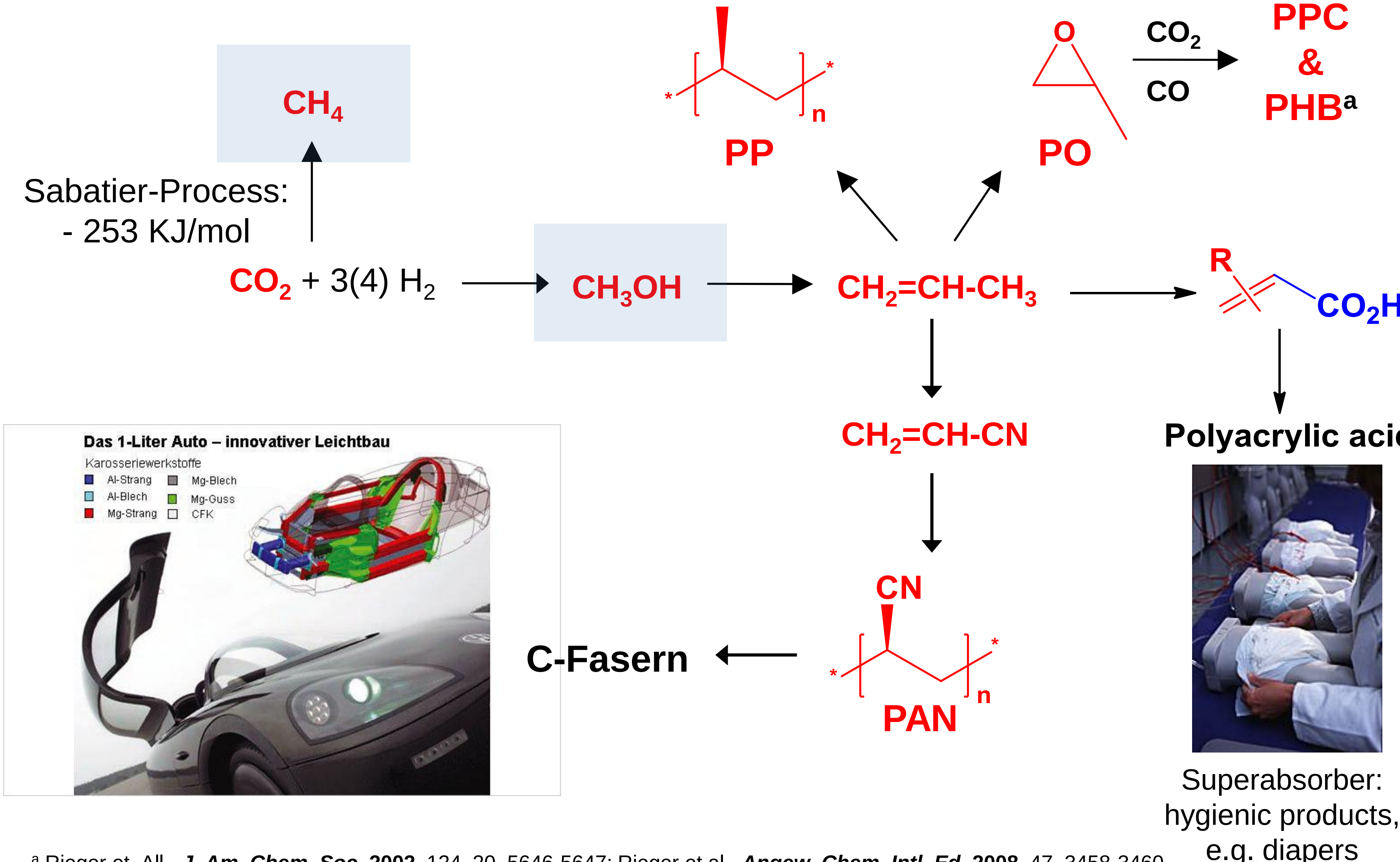
For The First Time: Commodities (ABS, *PS*) Without Oil

	PPC/PHB	ABS
	4800-5300	2200-3000
	0.3-0.9	0.4-0.7
	27-31	29-60
	170 (T_m)	95-105 (T_g)
	240	420

Dr. Greiner, *Siemens AG* **2011**

Pressemeldung Siemens „Laborpraxis“, 03. Mai 2012:
„Nachhaltiger Kunststoff mit Kohlendioxid aus Abgasen“

Polymers → Base Chemicals → Fuels
Mio to Giga to



[a] Rieger et. All., ***J. Am. Chem. Soc.*** **2002**, 124, 20, 5646-5647; Rieger et al., ***Angew. Chem. Intl. Ed***. **2008**, 47, 3458-3460

iC4: Integrated Carbon Capture, Conversion & Cycling

Die Chemie muss stimmen

Bundesministerium für Bildung und Forschung

TUM
WACKER
Clariant
THE LINDE GROUP Linde
e·on
MAN
SIEMENS
Fraunhofer IGB

iC4
Projektcluster

CO_2 Abtrennung & Reinigung		CO_2 Umwandlung & Nutzung	
		Methanisierung	Energie
Membranen	Ad/Ab-Sorbentien	Katalysatoren	Photokatalyse
<u>COOMem</u>	**<u>AdCOO</u>**	**<u>COOMeth</u>**	**<u>PhotoCOO</u>**
WACKER TUM FhG IGB Linde	Clariant TUM Siemens	WACKER MAN, TUM, E.ON Linde, Clariant	Clariant TUM

Infrastruktur zur Verteilung vorhanden

BMBF-Programm:
Technologien für Nachhaltigkeit und Klimaschutz, Chemische Prozesse und stoffliche Nutzung von CO_2
http://www.chemieundco2.de/de/157.php

Acknowledgement

Bundesministerium für Bildung und Forschung

DECHEMA
Gesellschaft für Chemische Technik und Biotechnologie e.V.

BASF
The Chemical Company

WACKER

Clariant

German-Canadian Research Network AM^{2}Net (DFG, NSERC)

SIEMENS

Bayer

MITSUBISHI CHEMICAL

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King Abdullah University of Science and Technology

P&G
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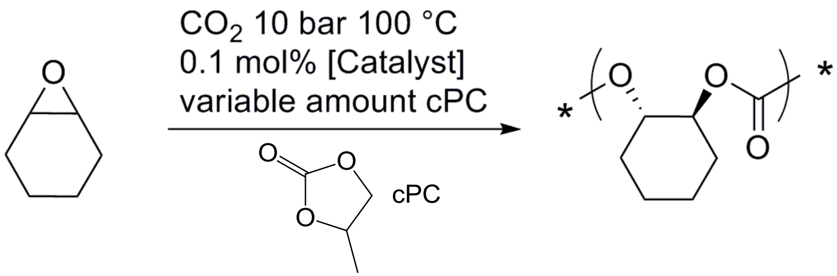
Roche

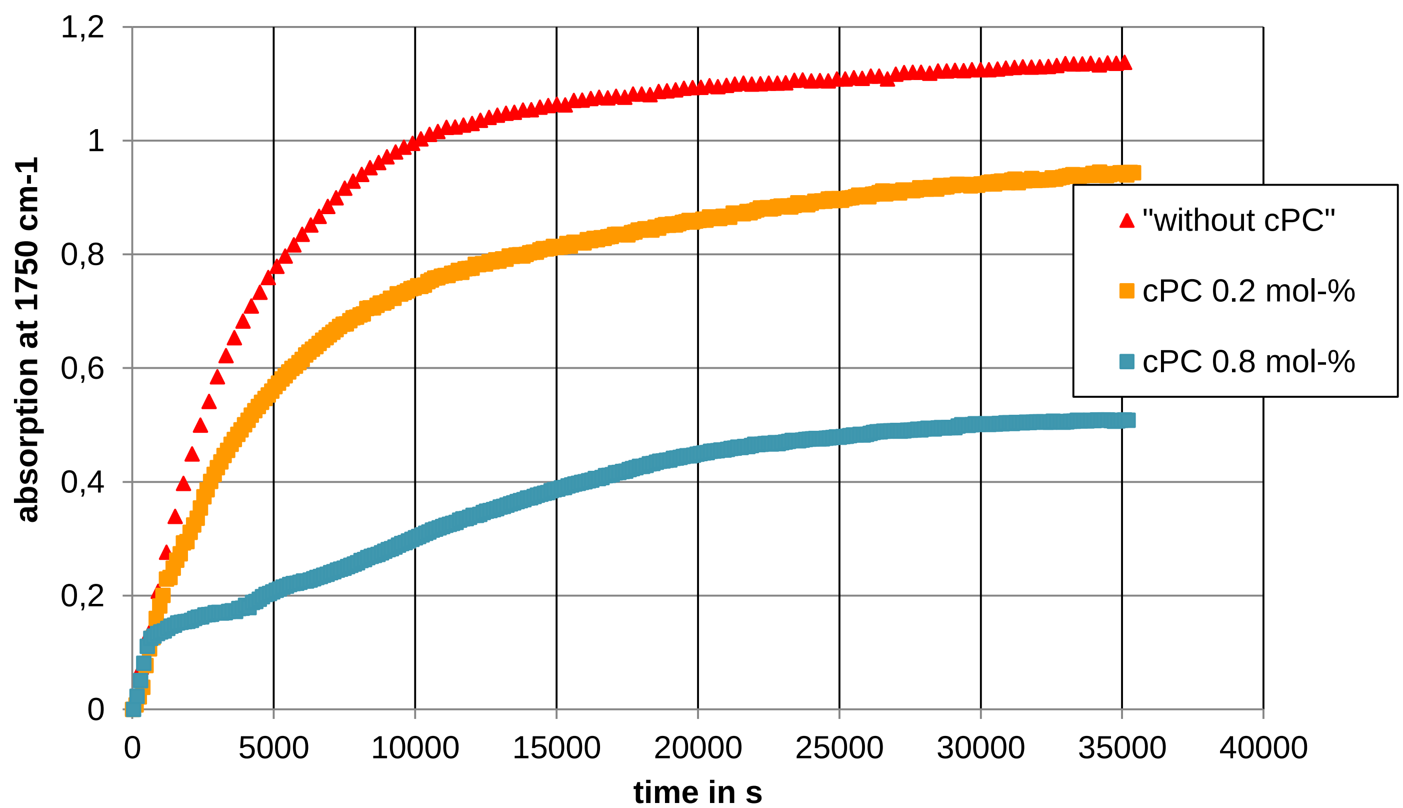
ExxonMobil

BOREALIS
SHAPING the FUTURE with PLASTICS

Product Inhibition

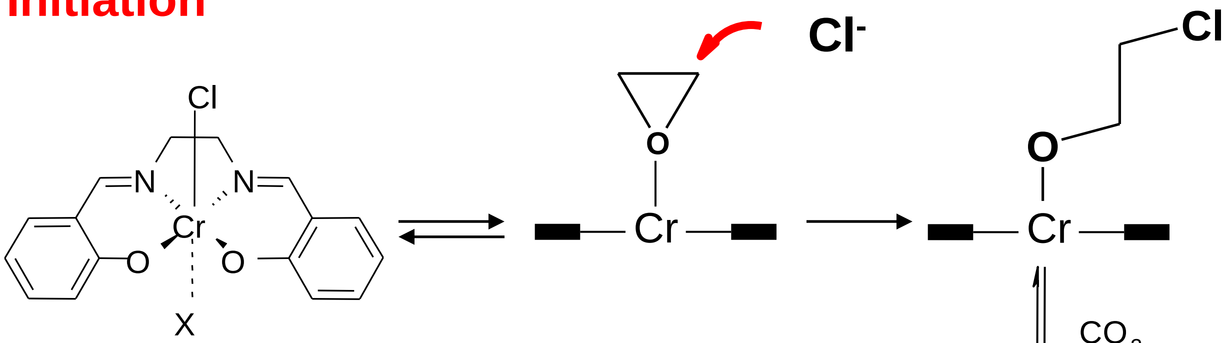
Reversible deactivation by cPC coordination



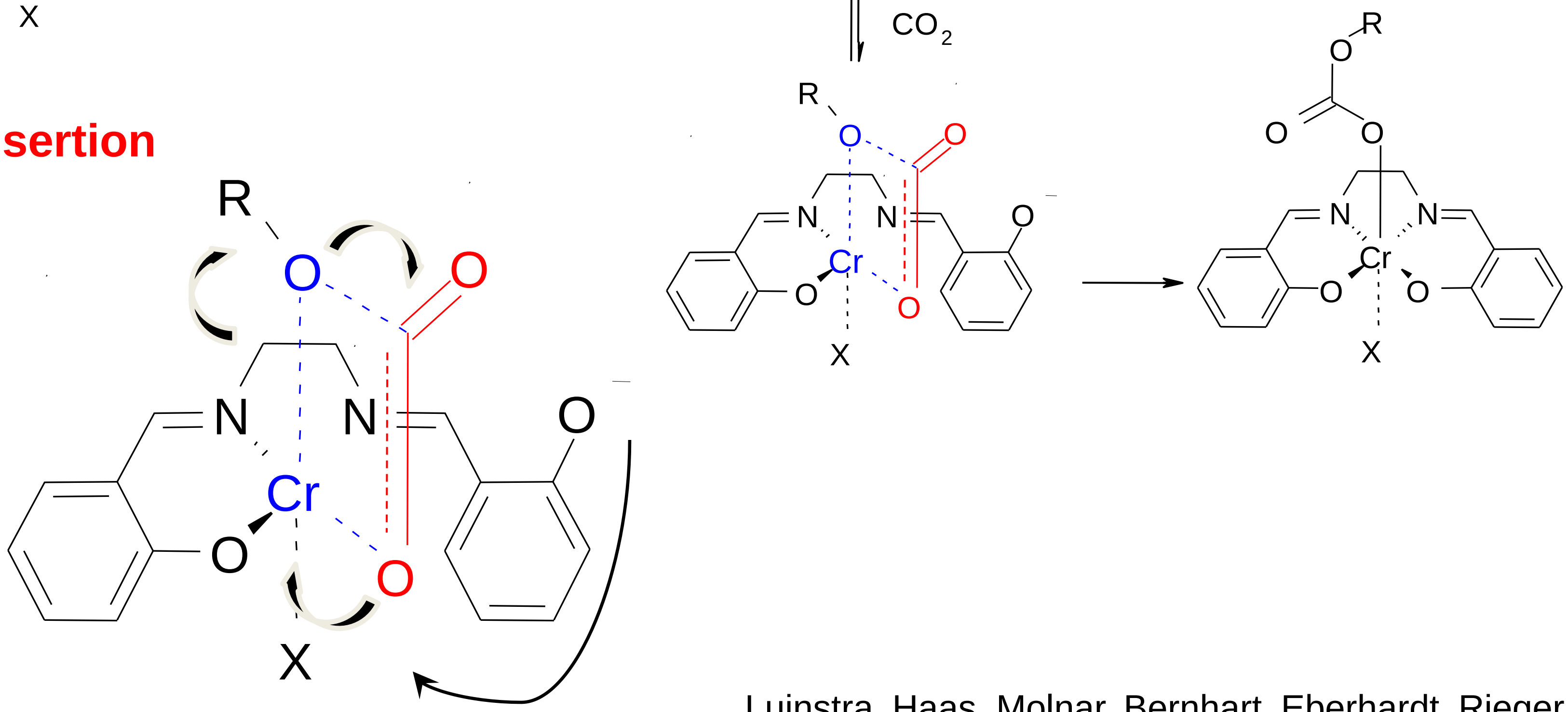


Complex Coordination Behavior

Initiation



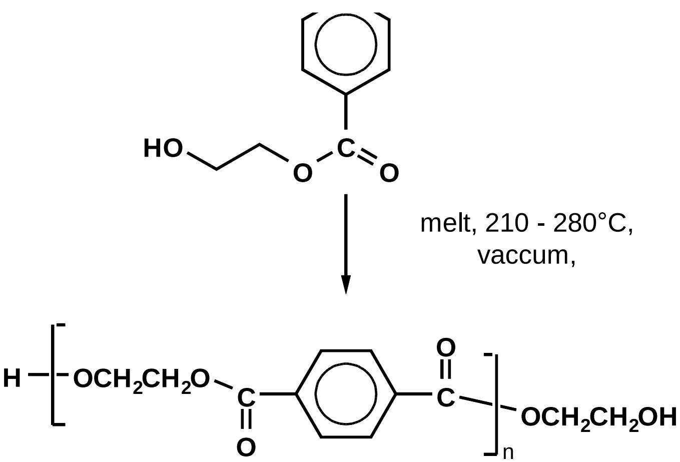
CO_2 Insertion



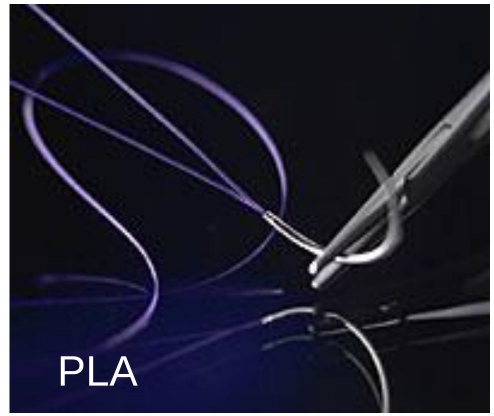
Luinstra, Haas, Molnar, Bernhart, Eberhardt, Rieger,
Chem. Eur. J. **2005**, 11, 6298

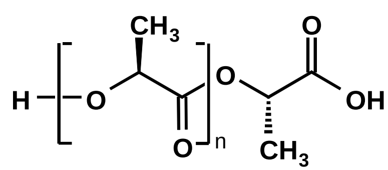
Polyethyleneterephthalate Polylactide **Polyhydroxybutyrate**

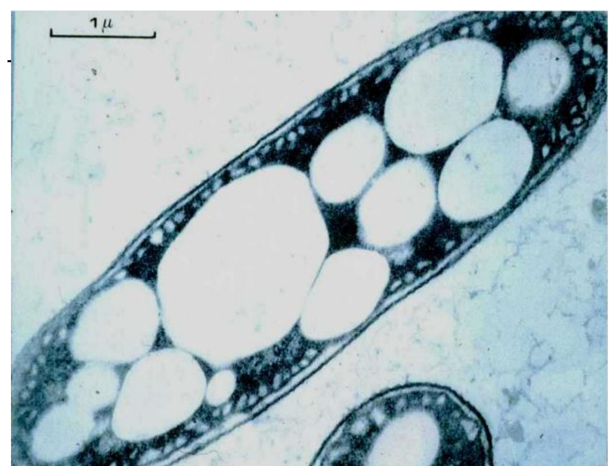
PET: Polykondensation



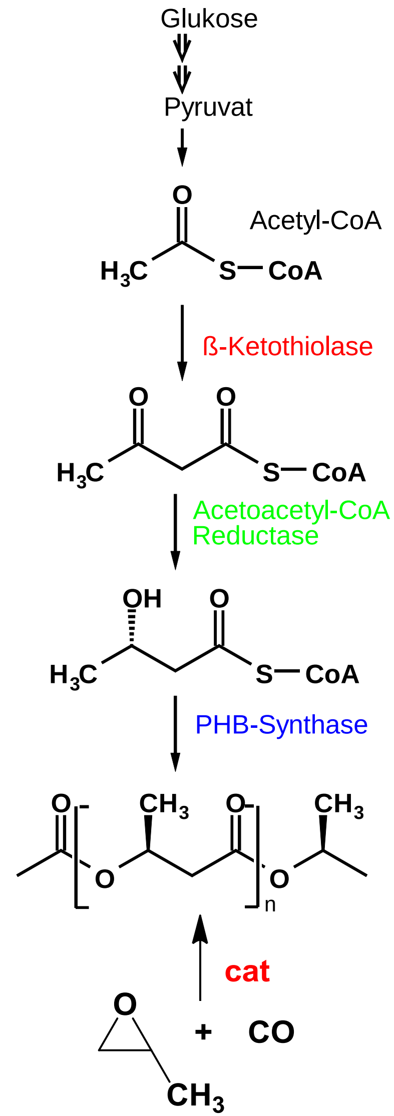
PLA: Ring opening





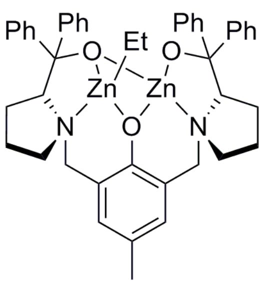


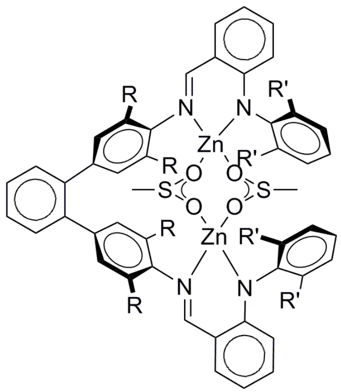
PHB: Bio-synthesis



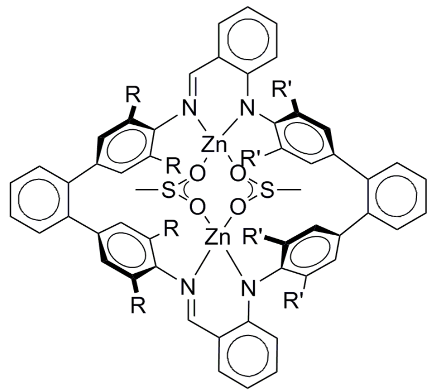
Cooperative Mechanism ?

- dinuclear complexes (only CHO!)



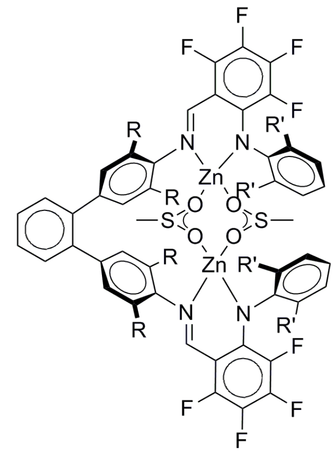


"open"

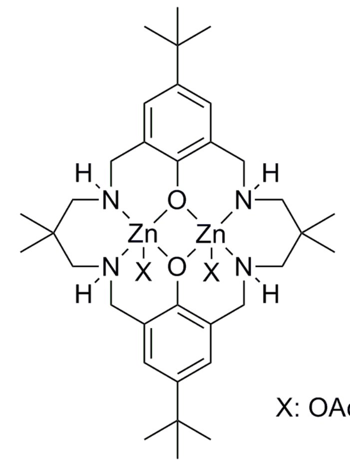


"closed"

R = Me, Et, *i*Pr
R'= Me, Et, *i*Pr



R = Me, Et, *i*-Pr
R'= Me, Et, *i*-Pr

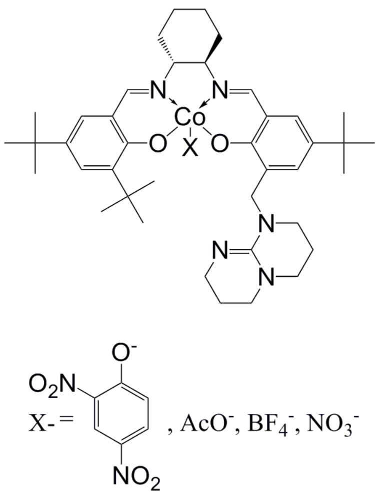


X: OAc^-

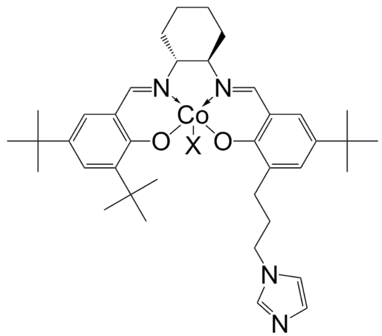
Ding 2005	Lee 2005	Lee 2005	Lee 2006	Williams 2009
TOF: 140 h^{-1}	TOF = 200	TOF = 0	TOF = 2.860	TOF = 25
			less PCHC	1 bar !

S. Klaus, M. W. Lehenmeier, C. E. Anderson, B. Rieger, Coord. Chem. Rev. 2011

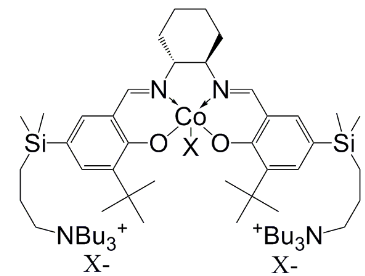
Ionic Structures



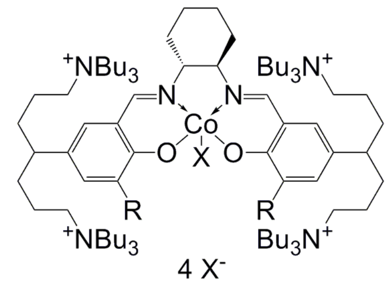
Lu 2009
TOF = 7.319 h^{-1}



Lu 2009
TOF = 7



Lu 2009
TOF = 3.500



R = t-Bu, *i*-Pr, Me

Lee 2007
TOF = 26.000

S. Klaus, M. W. Lehenmeier, C. E. Anderson, B. Rieger, *Coord. Chem. Rev.* 2011.