DFT study on the cobalt(III) catalysts for CO_2/epoxide copolymerization

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dr Monika Srebro

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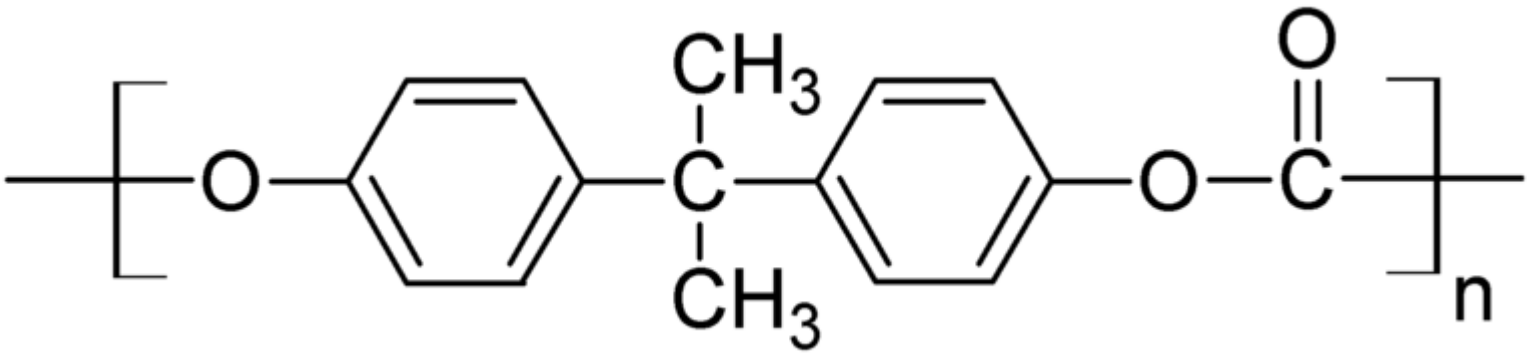
Polycarbonates



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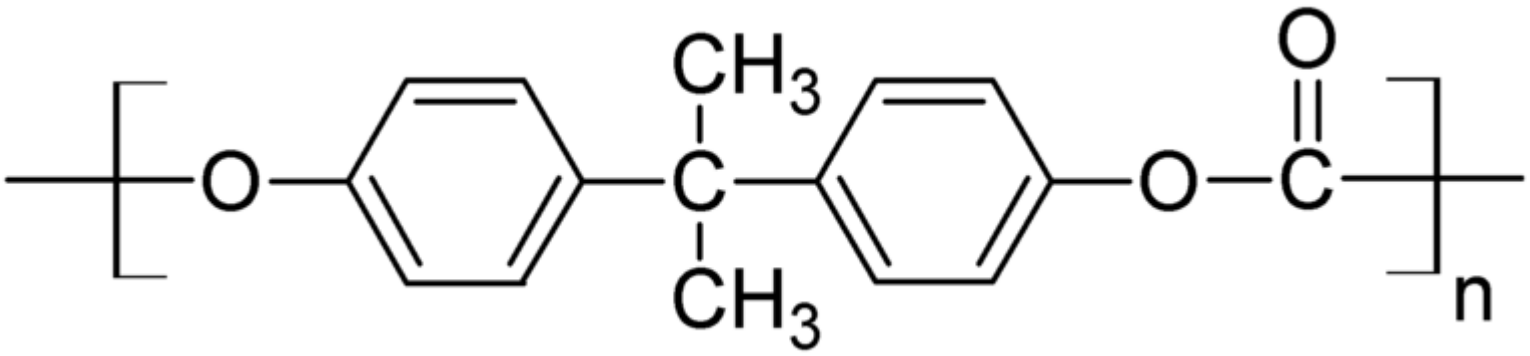

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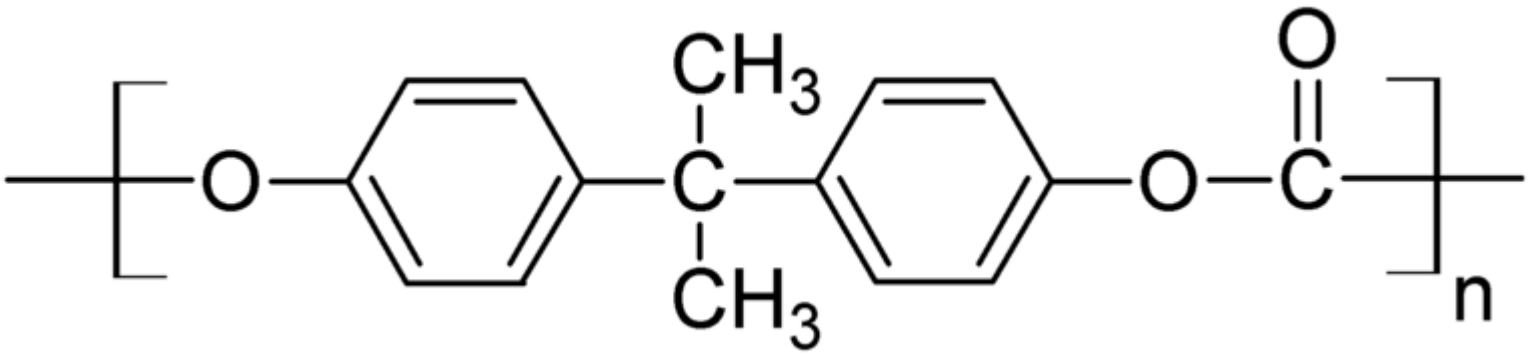

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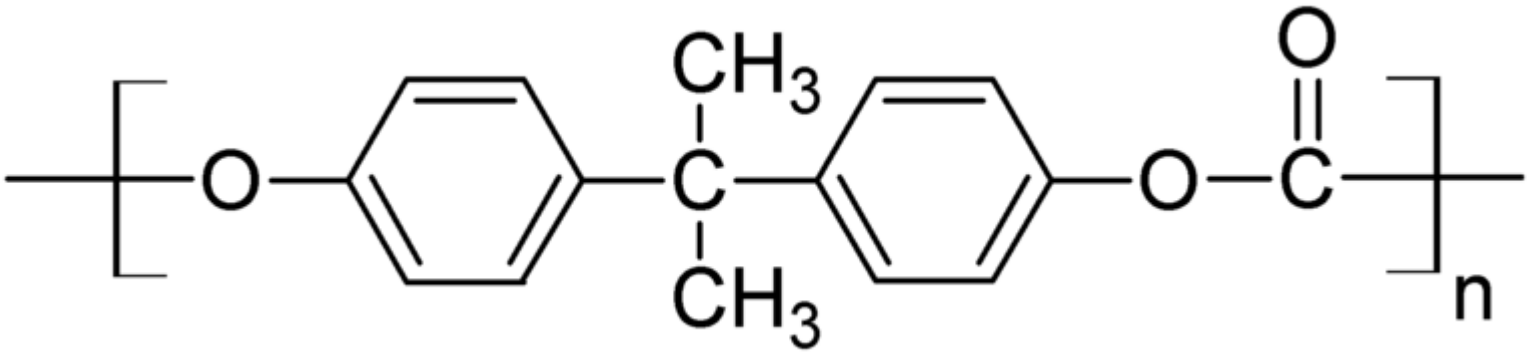

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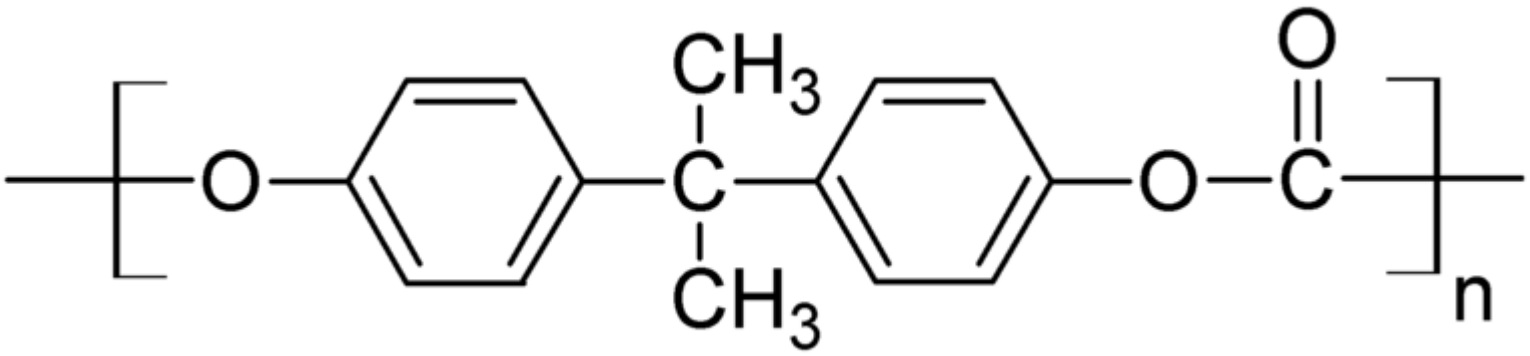

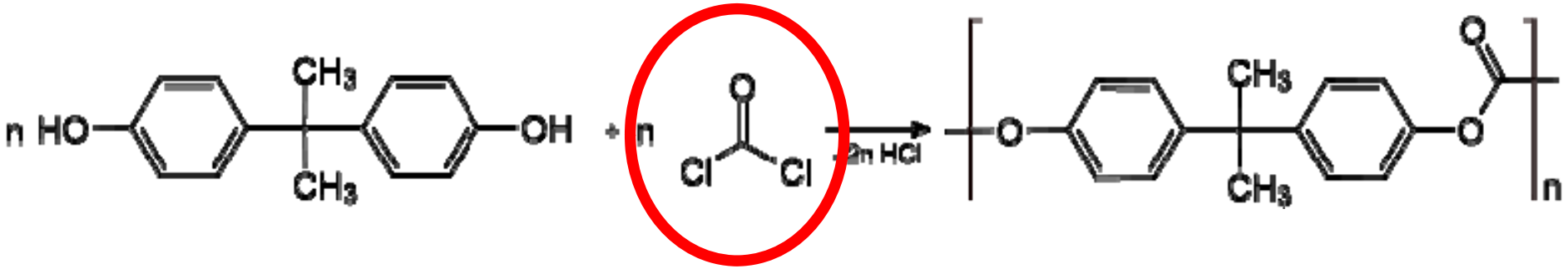

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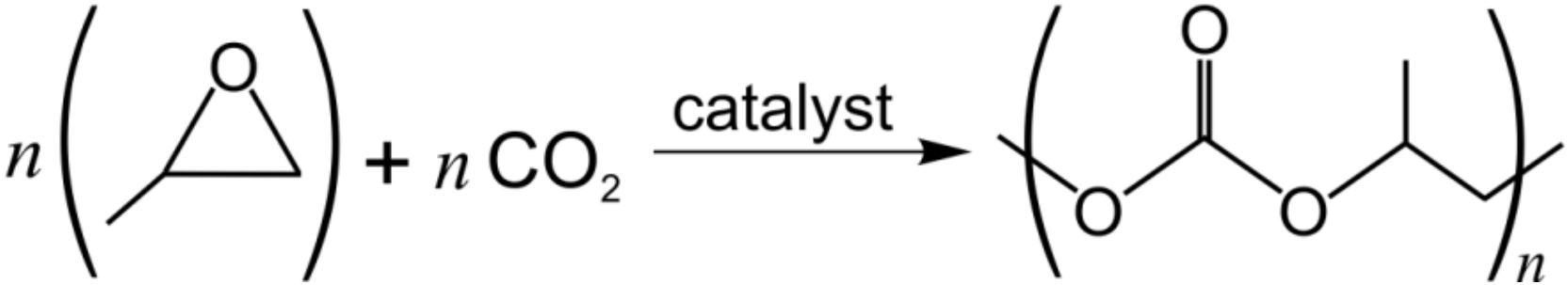

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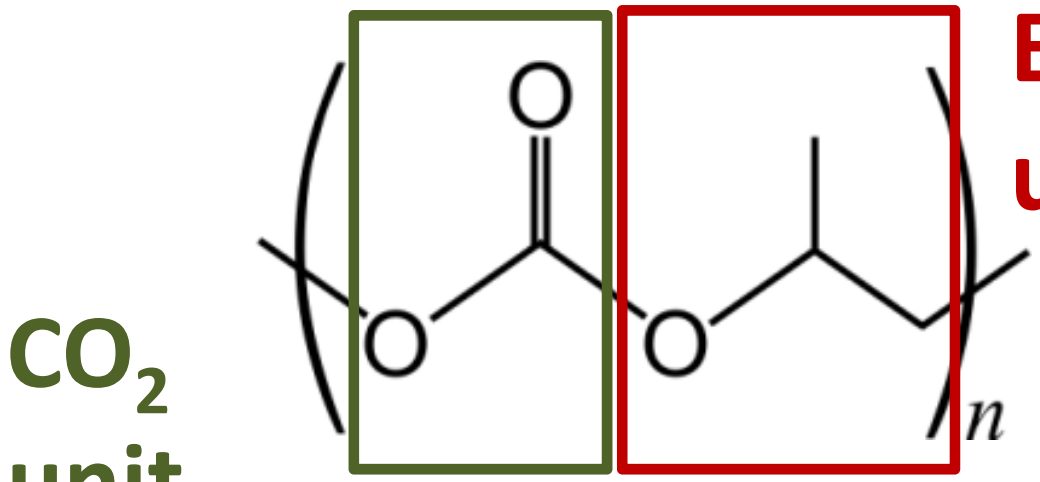
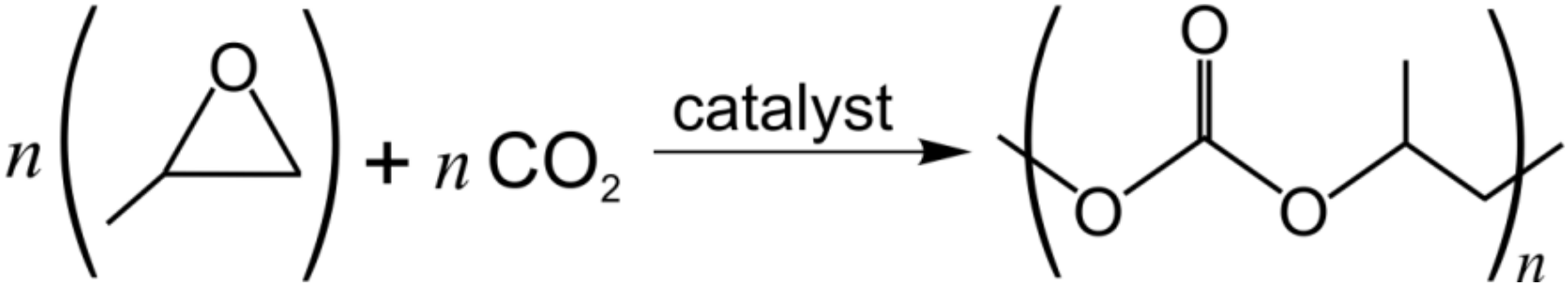
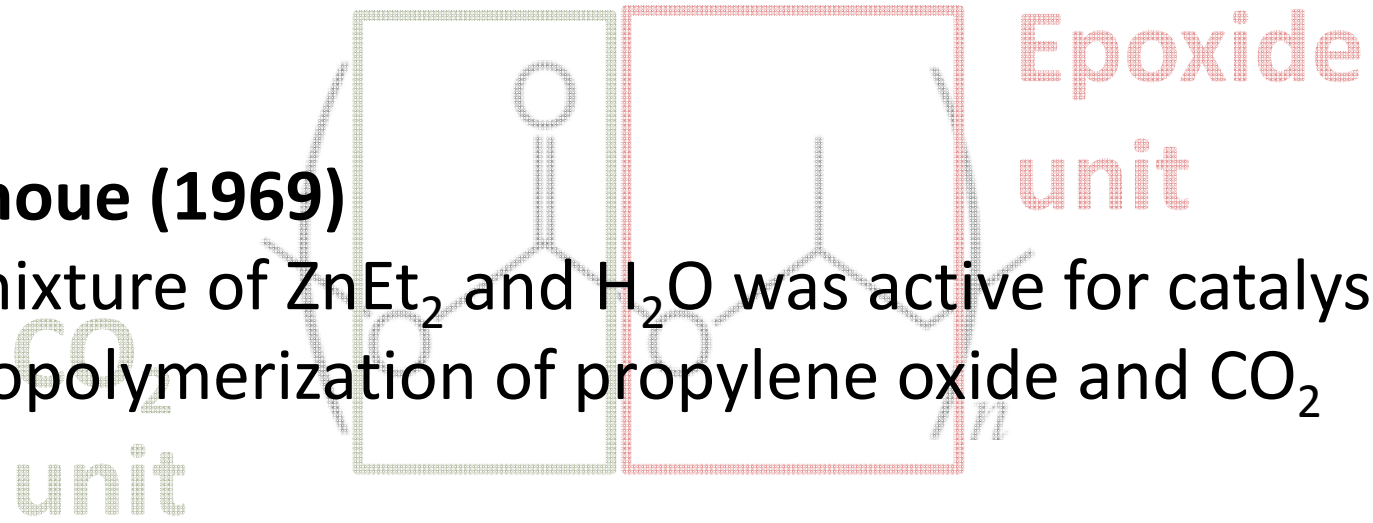


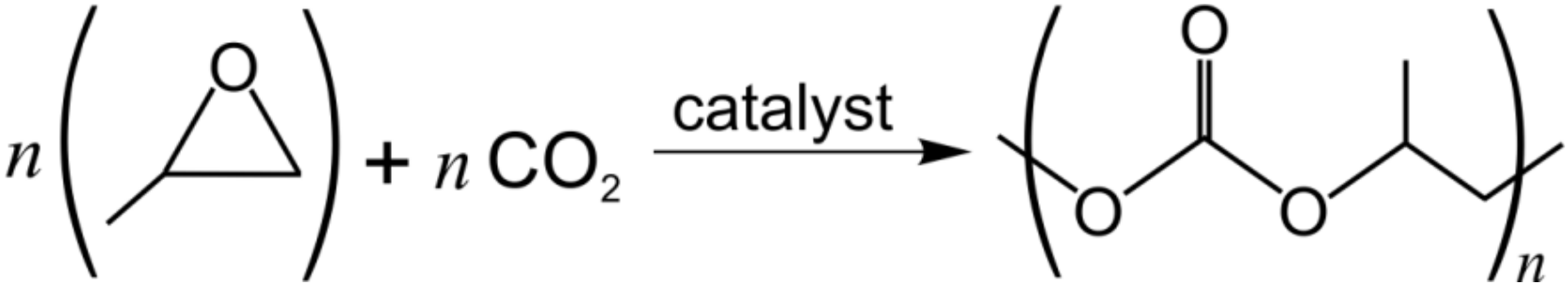


Catalytic systems



Inoue (1969)

mixture of $ZnEt_2$ and H_2O was active for catalysing copolymerization of propylene oxide and CO_2



Catalytic systems

Inoue (1969) **TOF: 0.12 h^{-1}**

$ZnEt_2/H_2O$

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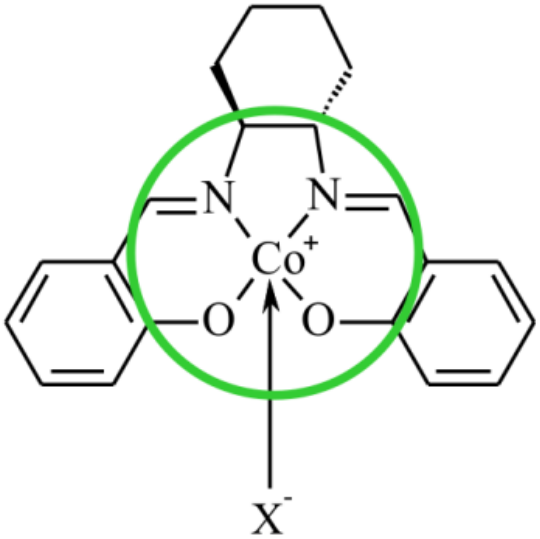
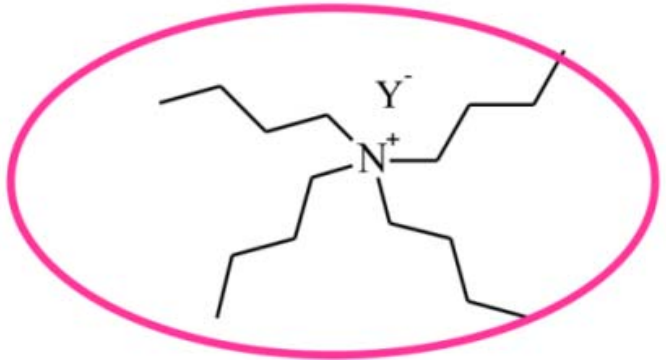
Coates (2003) **TOF: 17-81 h^{-1}**



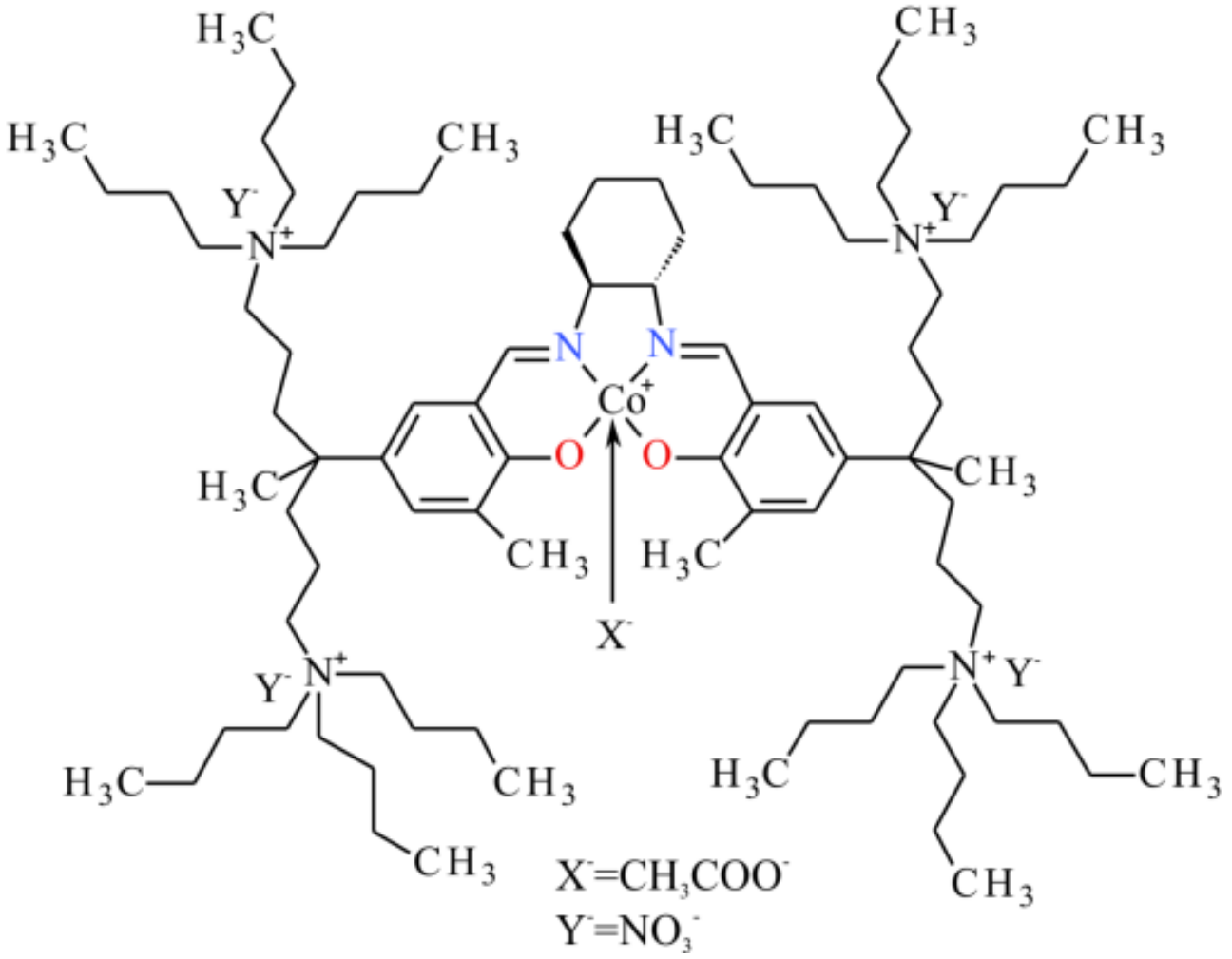


Catalytic systems

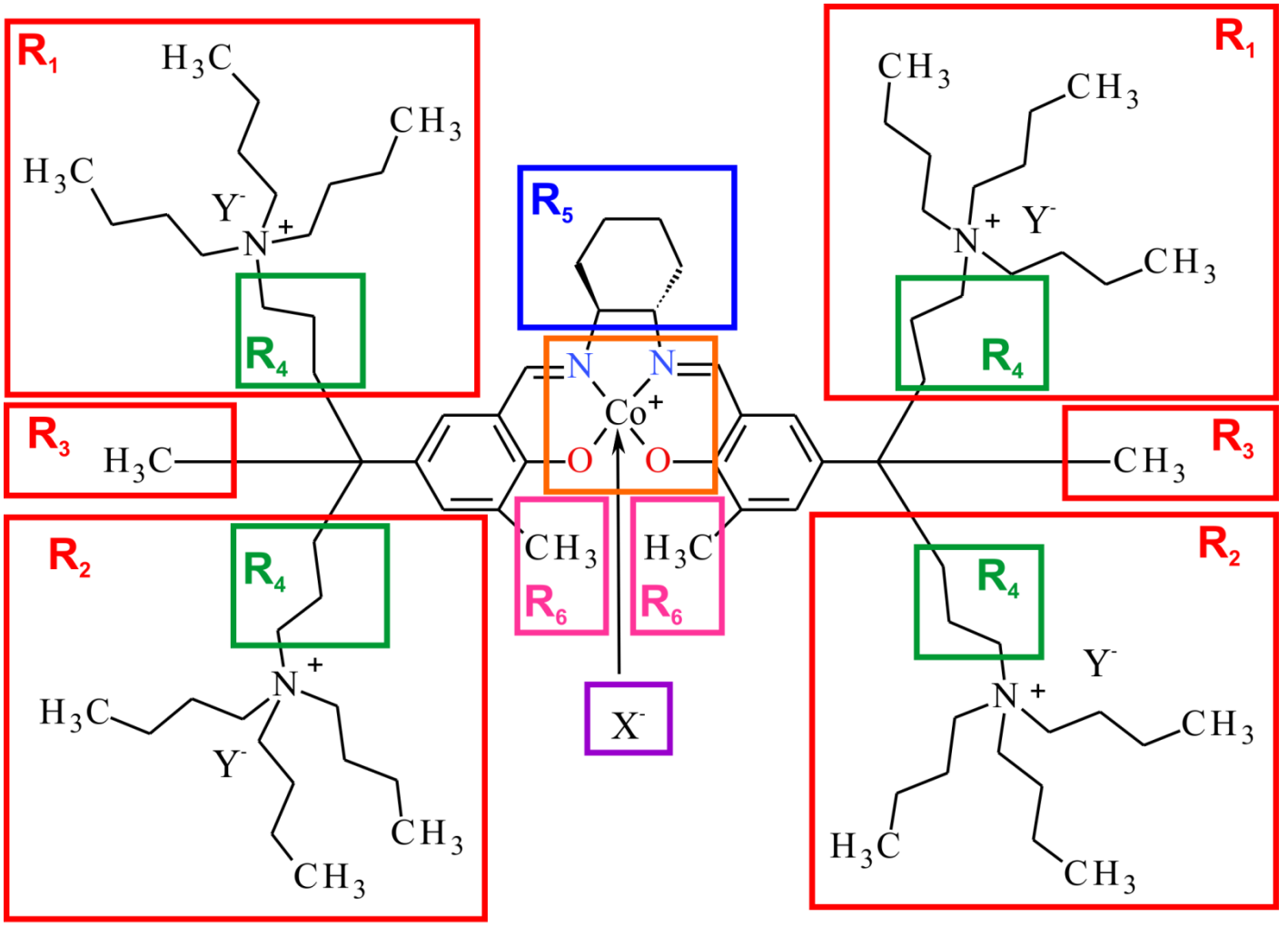
Inoue (1969)	**TOF:**	**0.12 h^{-1}**
Coates (2003)	**TOF:**	**17-81 h^{-1}**
Bun Yeoul Lee (2009)	**TOF:**	**16 000 h^{-1}**

Catalytic systems – most active catalyst

Bun Yeoul Lee (2009) TOF: 16 000 h^{-1}



Catalytic systems – hypothetical key factors

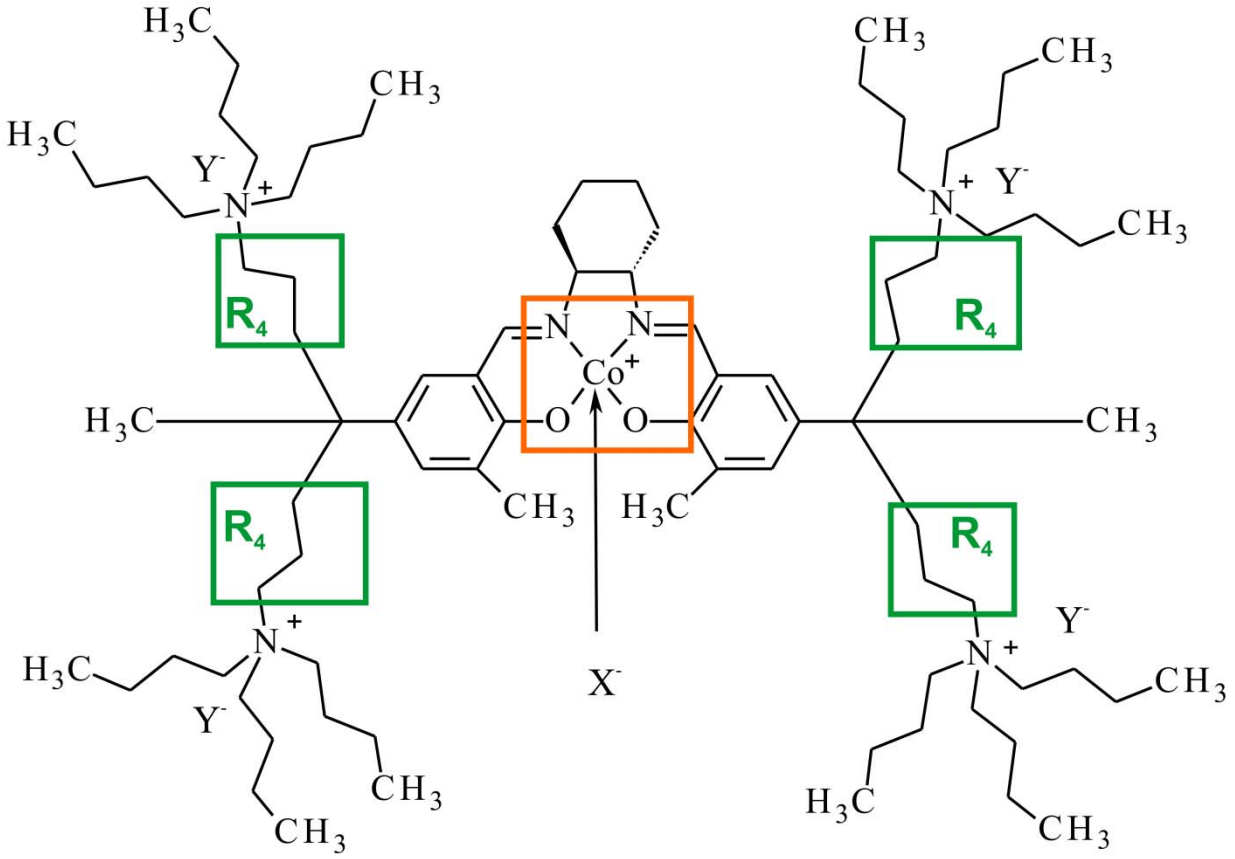


$X^-=CH_3COO^-$

$Y^-=NO_3^-$

Catalytic systems – hypothetical key factors

How does **the length of the alkyl chain** linking the N^+-salt with the salen ligand **affect stability** of structure?



$X^-=CH_3COO^-$

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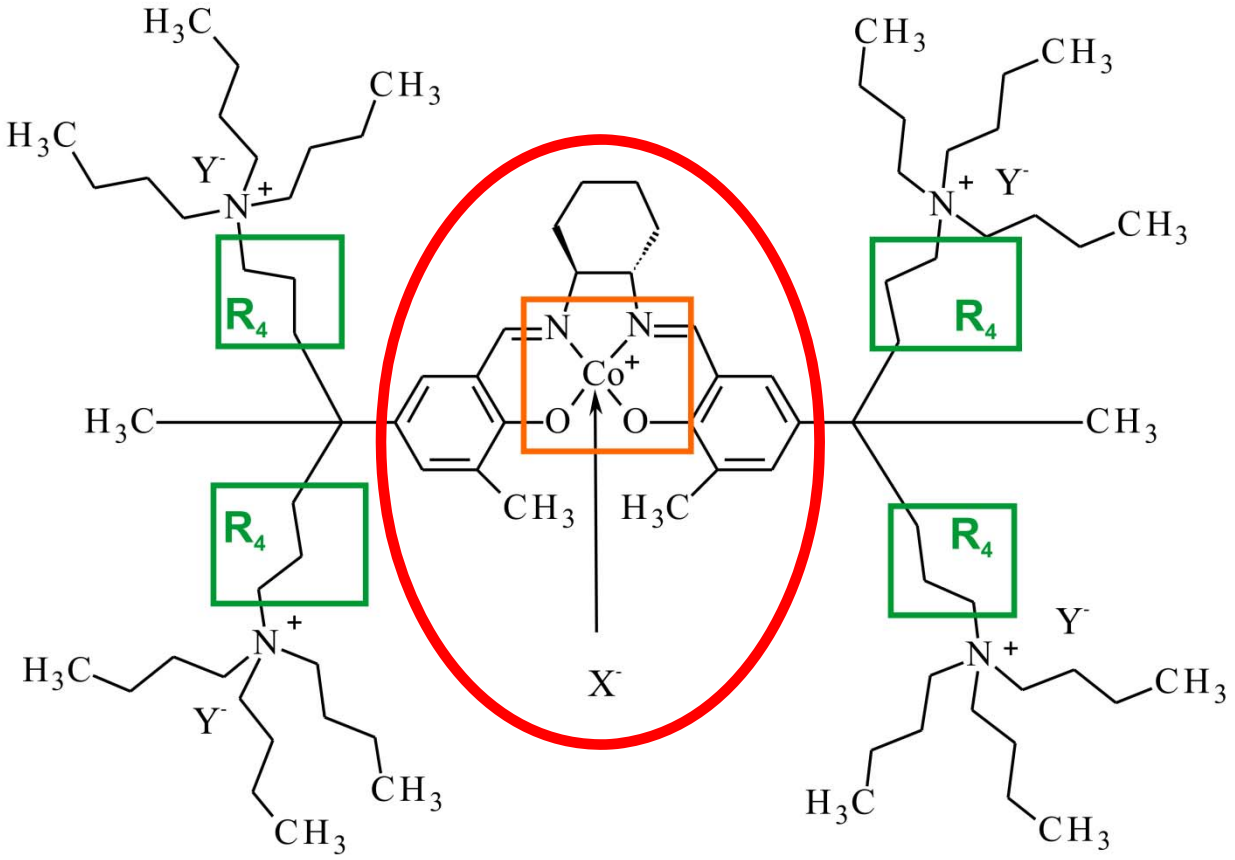
Catalytic systems – first model



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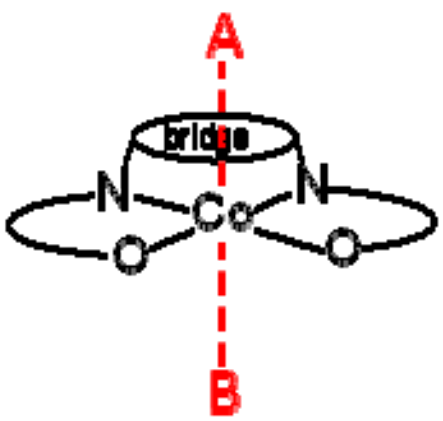
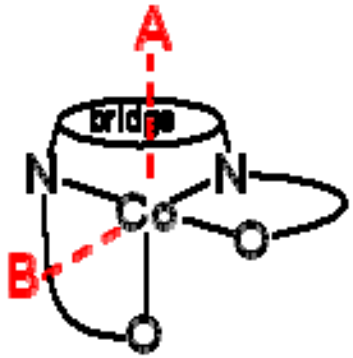
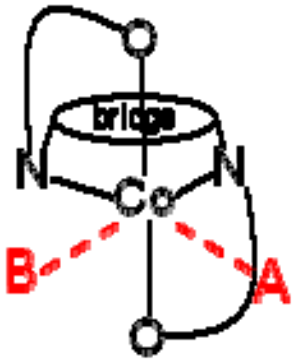


trans

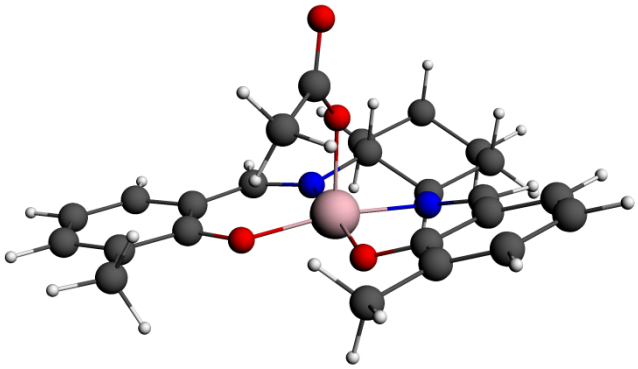


cis-β

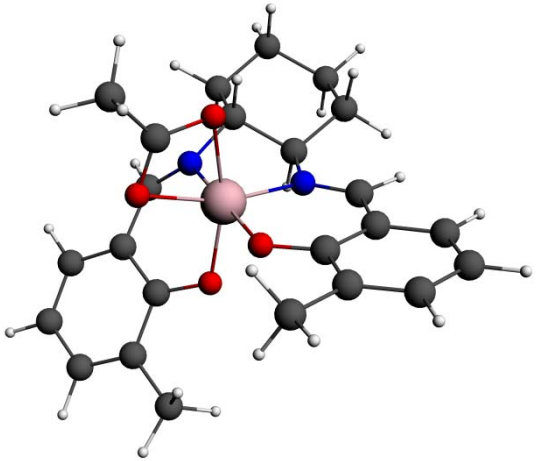


cis-α

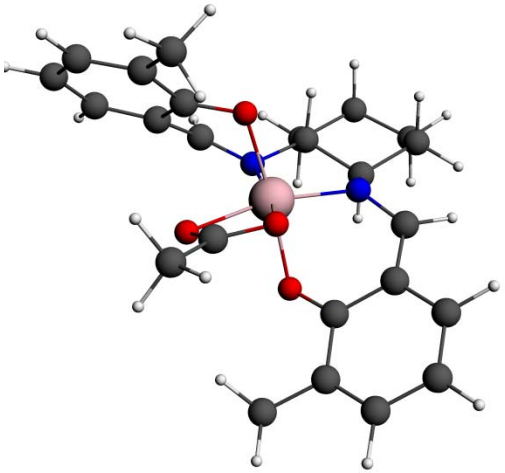
I



8.66

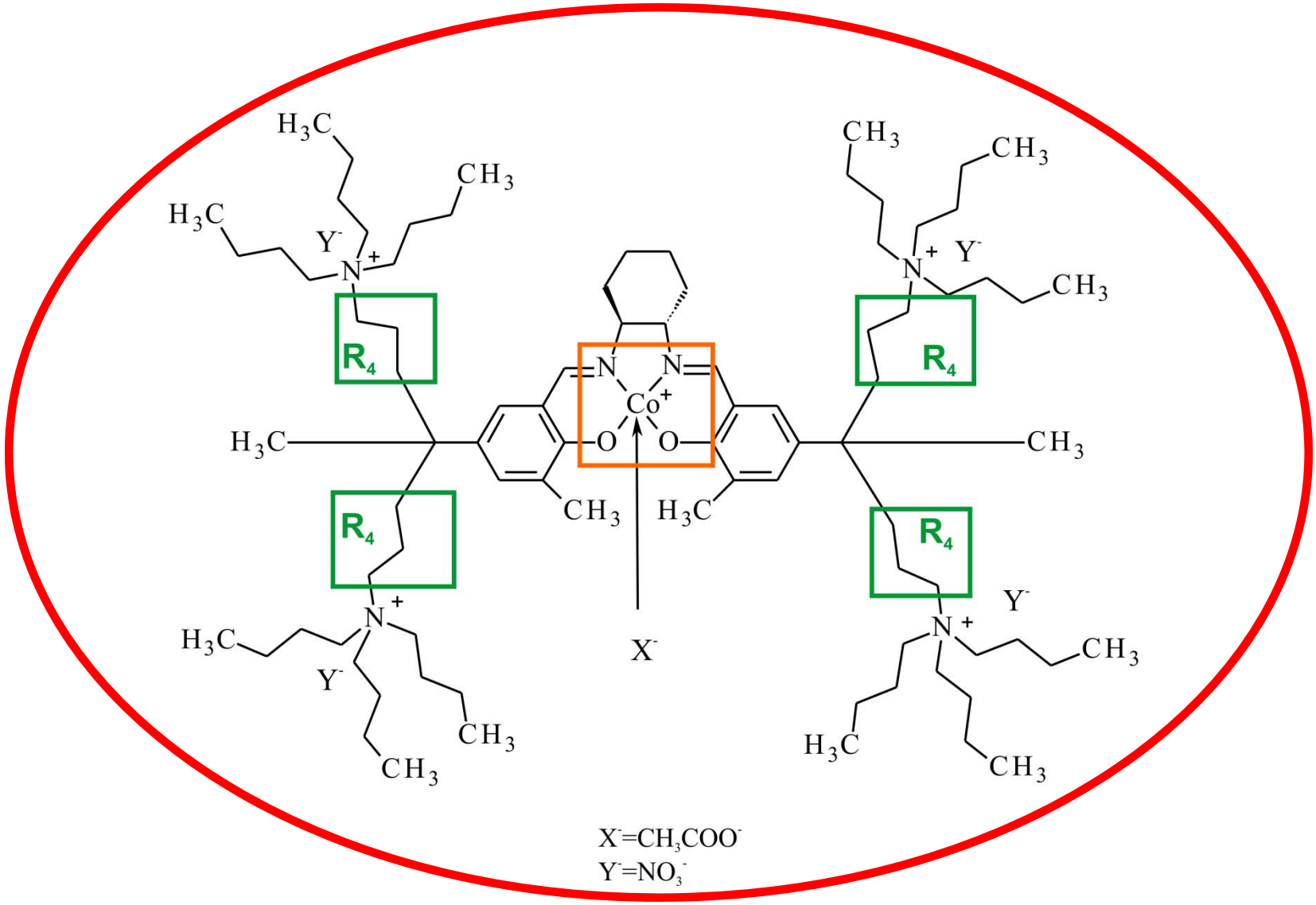


0.00



32.35

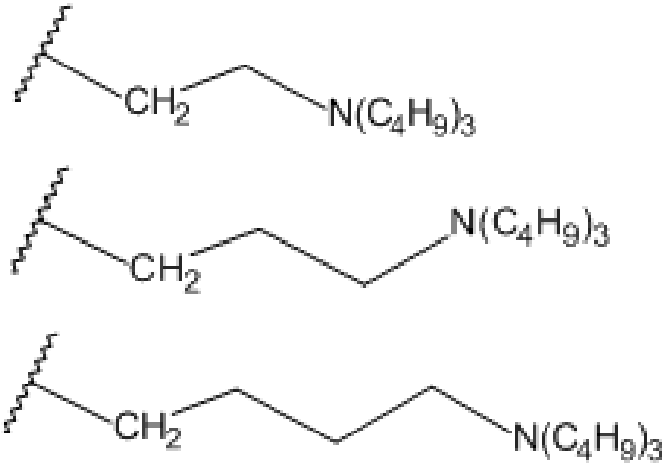
Catalytic systems – advanced models

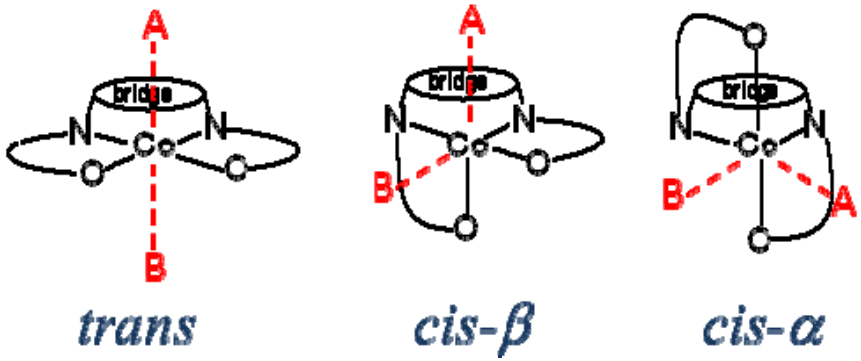


Catalytic systems – static calculations

	trans	cisβ	cisα
I	8.66	0.00	32.35
II	11.08	0.00	21.96
III	10.74	0.00	32.38
IV	44.13	0.00	32.42

without N^+-chains

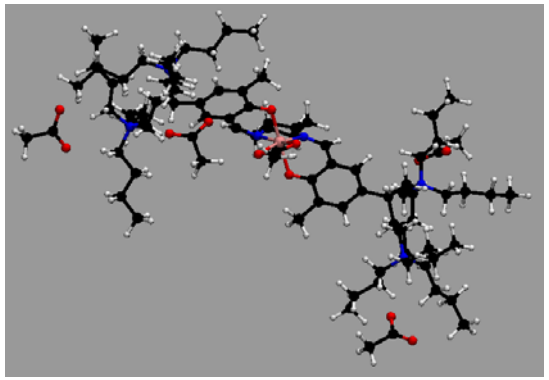
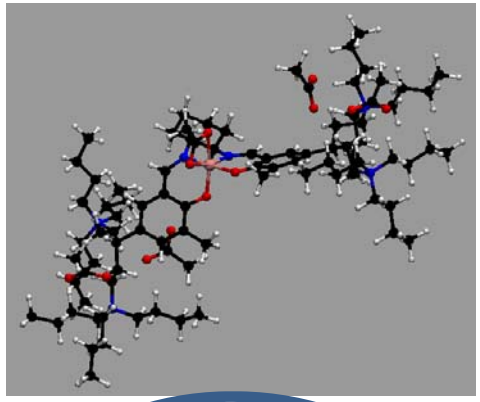
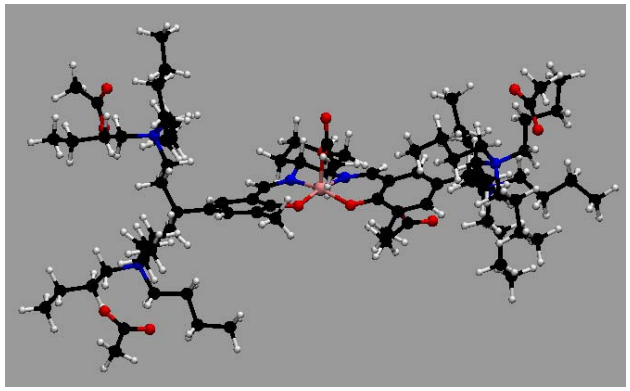
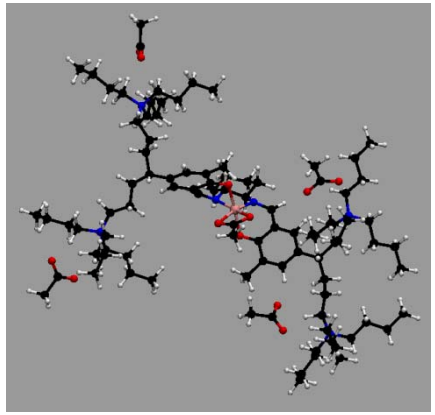
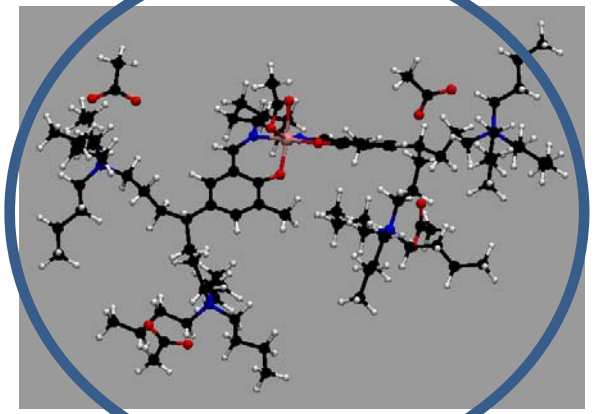
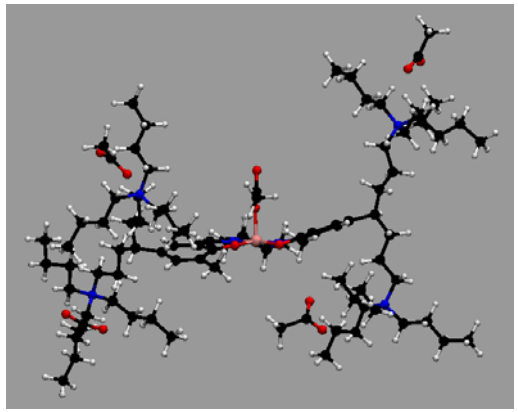
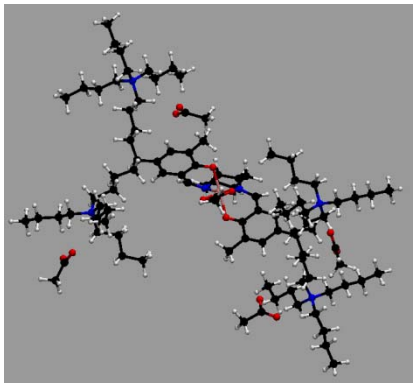
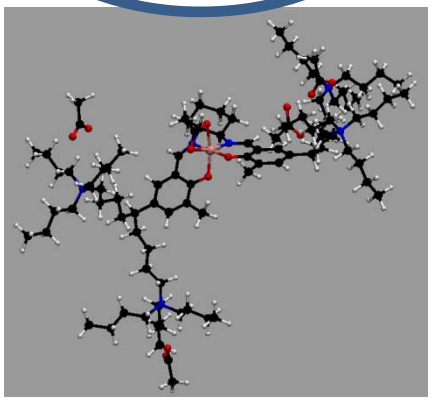
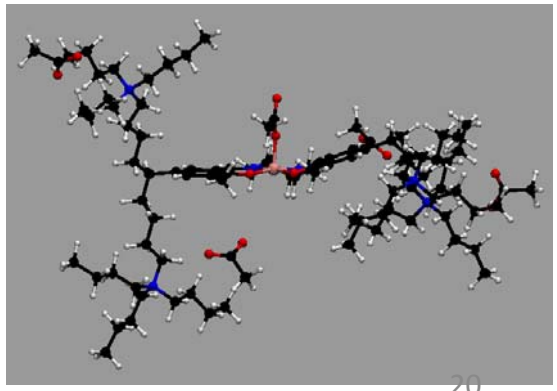




CP2K program (static calculations)

for all elements DZVP basis was used; XC functional Becke88Perdew+Grimme3

box with edge equal to 40 Å ; cut off 260;

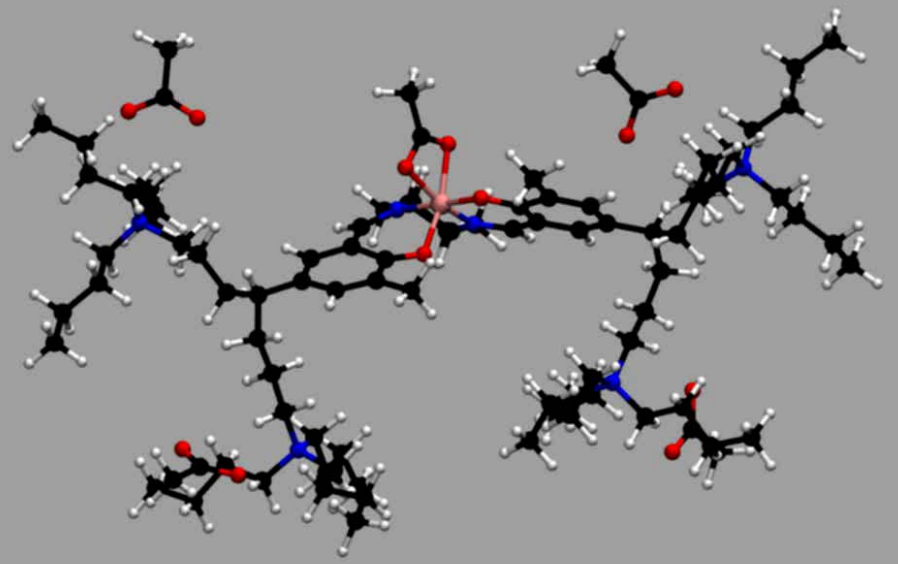
	cisα	cisβ	trans
II			
	21.96	0.00	11.08
III			
	32.38	0.00	10.74
IV			
	32.42	0.00	44.13

Systems with four N^+-salts – DYNAMIC picture

CP2K program (dynamic and static calculations)
for all elements DZVP basis was used; XC functional Becke88Perdew+Grimme3
box with edge equal to 40 Å ; cut off 260;
dynamic calculations T=300K

III cisβ

6 ps of MD simulation
22 years on single CPU
} movie 18 s



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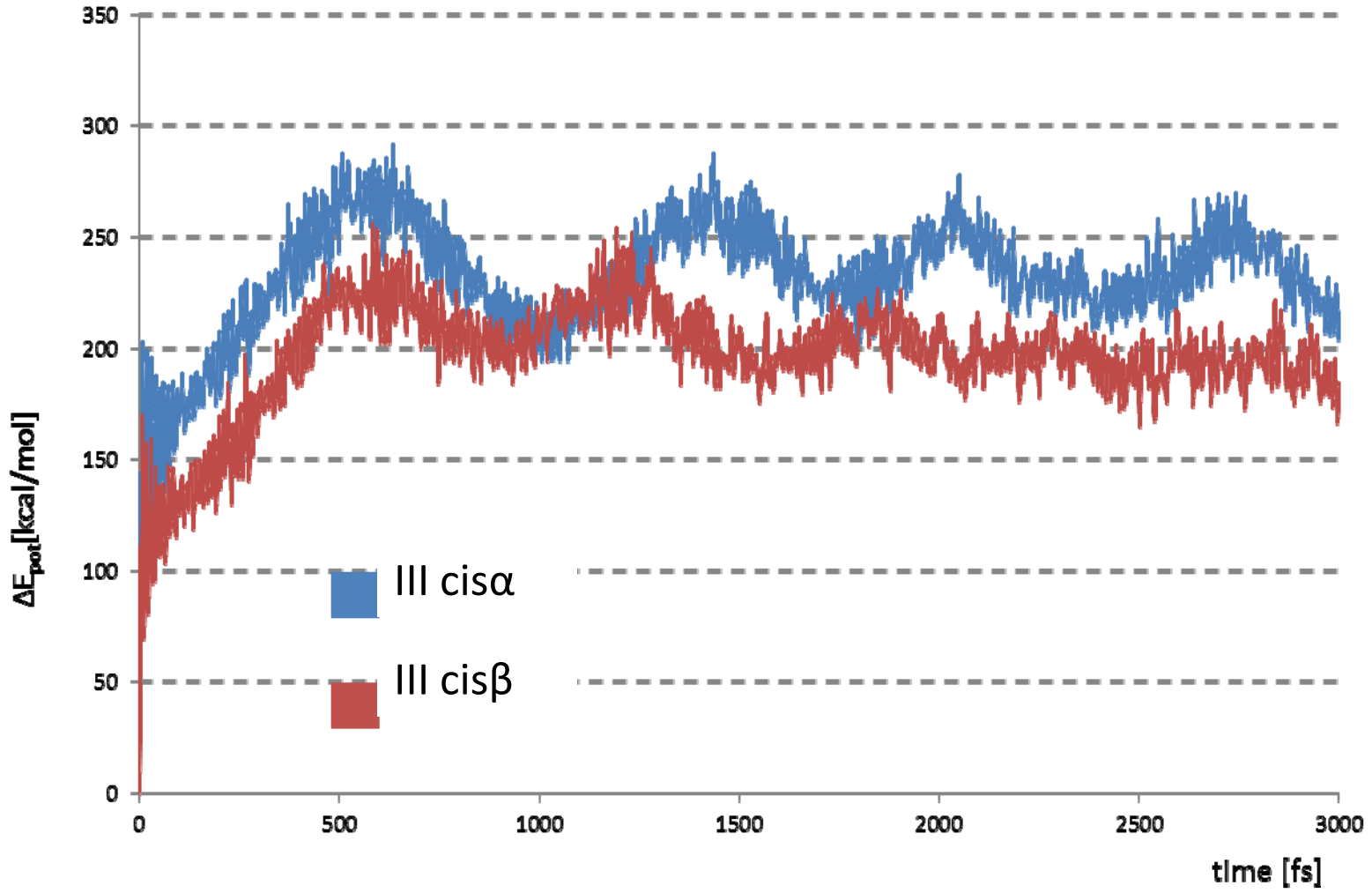
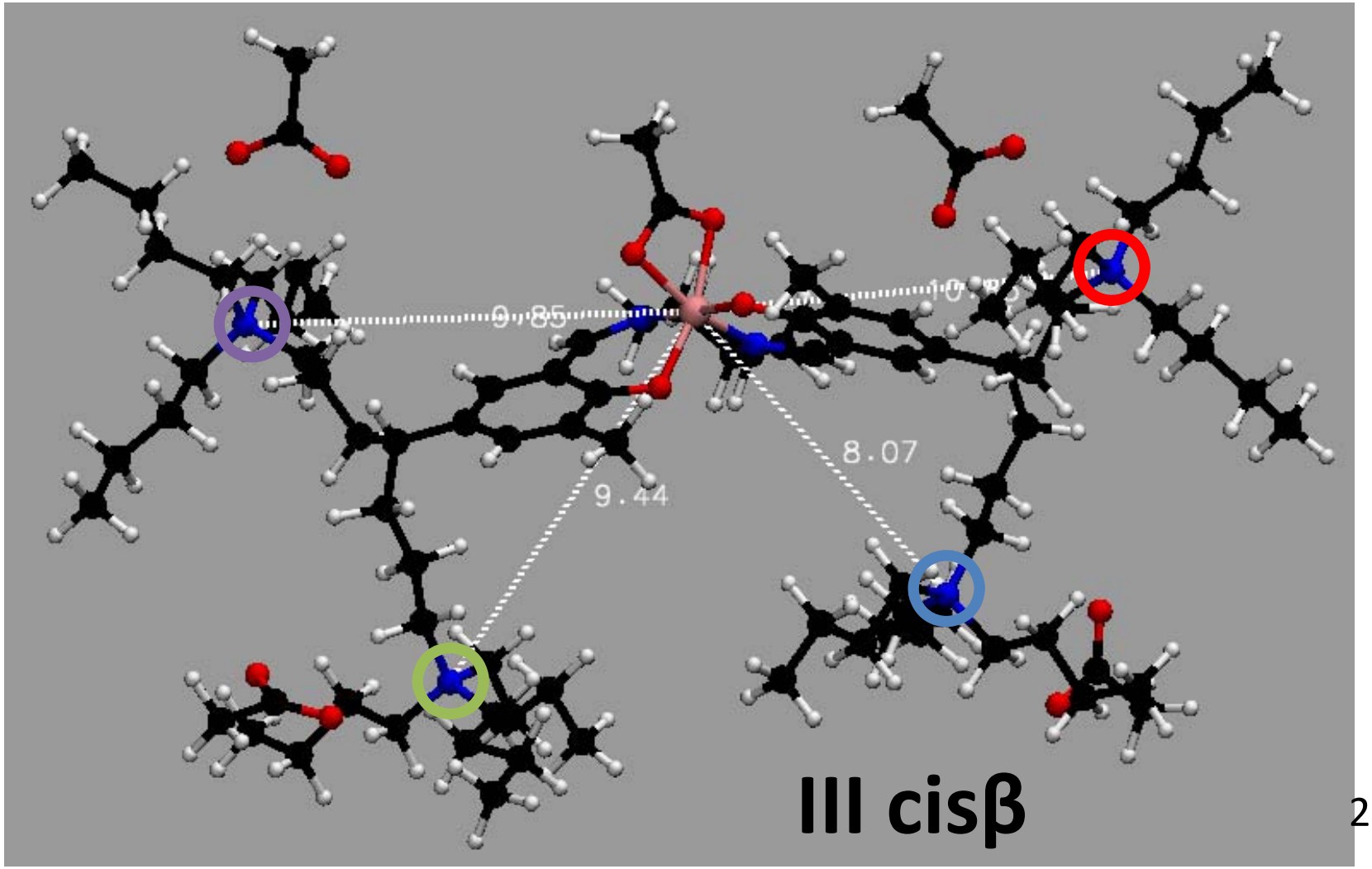


Systems with four N^+-salts – DYNAMIC picture

How does **the length of the alkyl chain** linking the N^+-salt with the salen ligand **affect stability** of structure?



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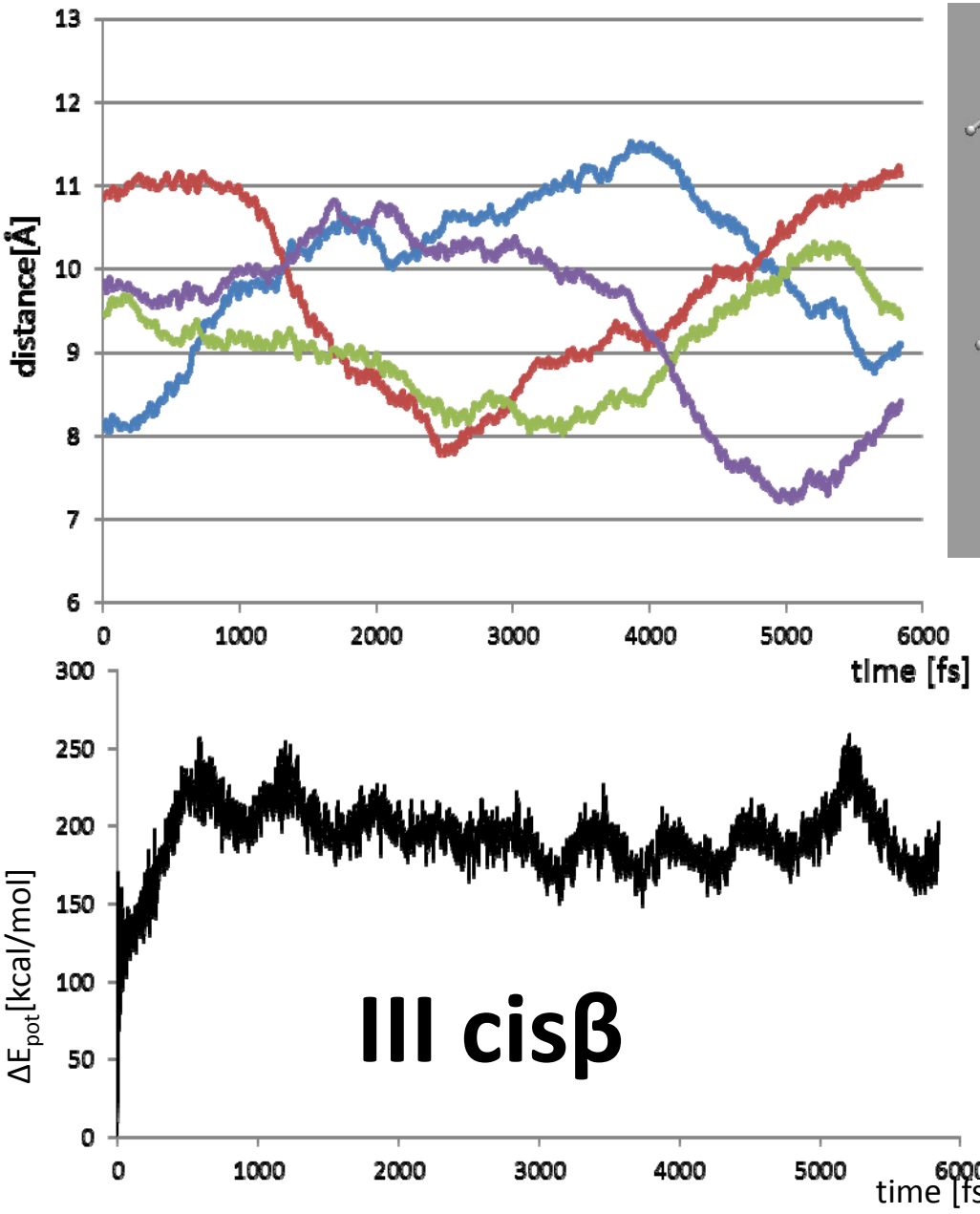
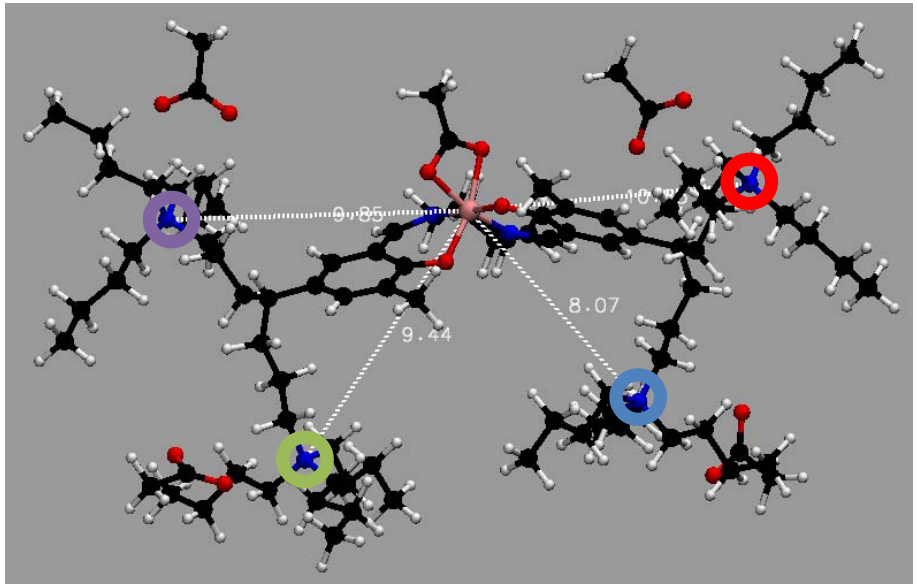


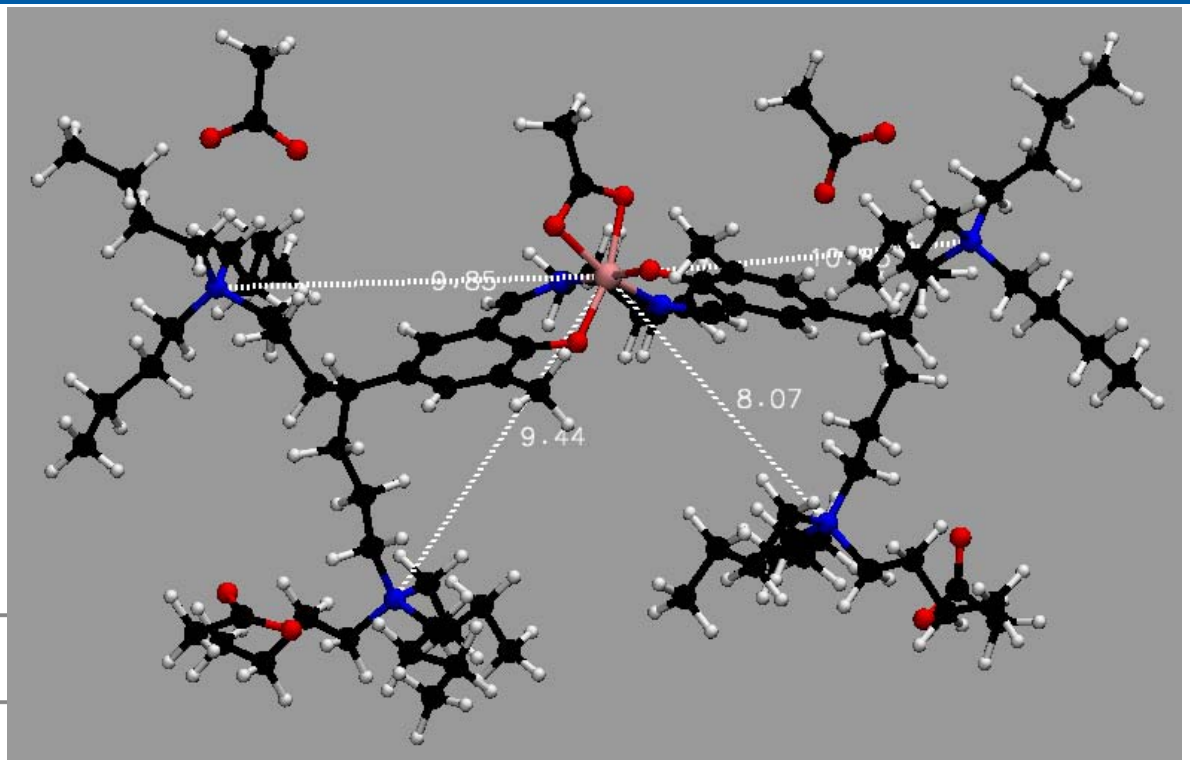


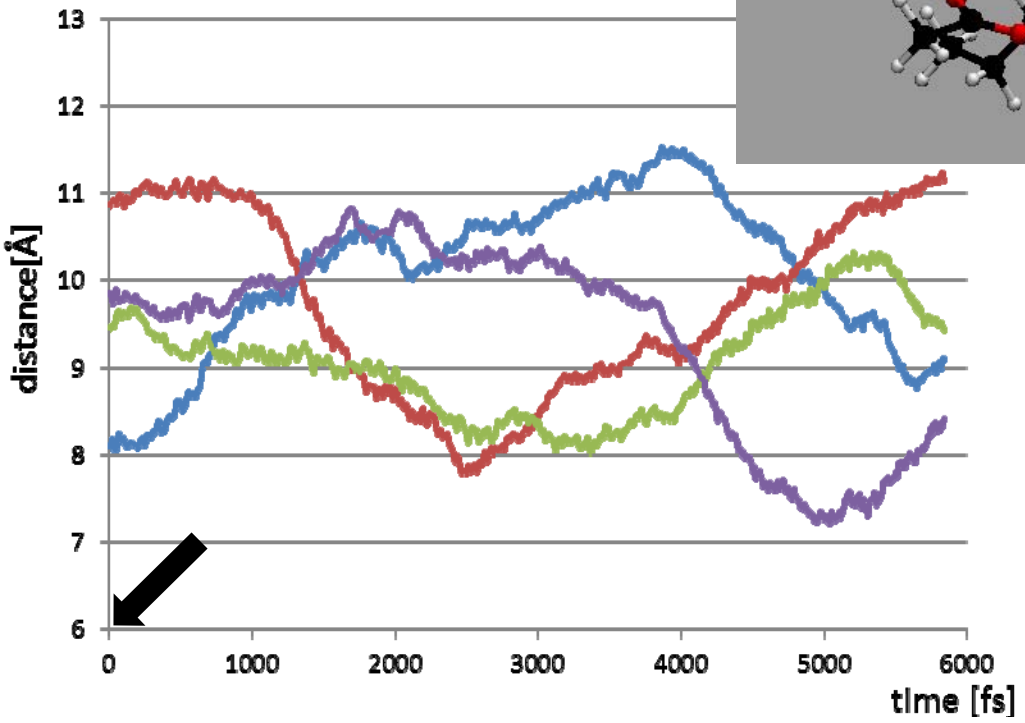
distances between cobalt atom and nitrogen atoms from chains with $(Bu)_3N^+$ group – colors on the picture corresponds do the colors on the graph (top);
changes in potential energy along MD trajcetory (bottom graph)

Systems with four N^+-salts – DYNAMIC picture

III cisβ

starting geometry t=0





N-Co 9.85 A

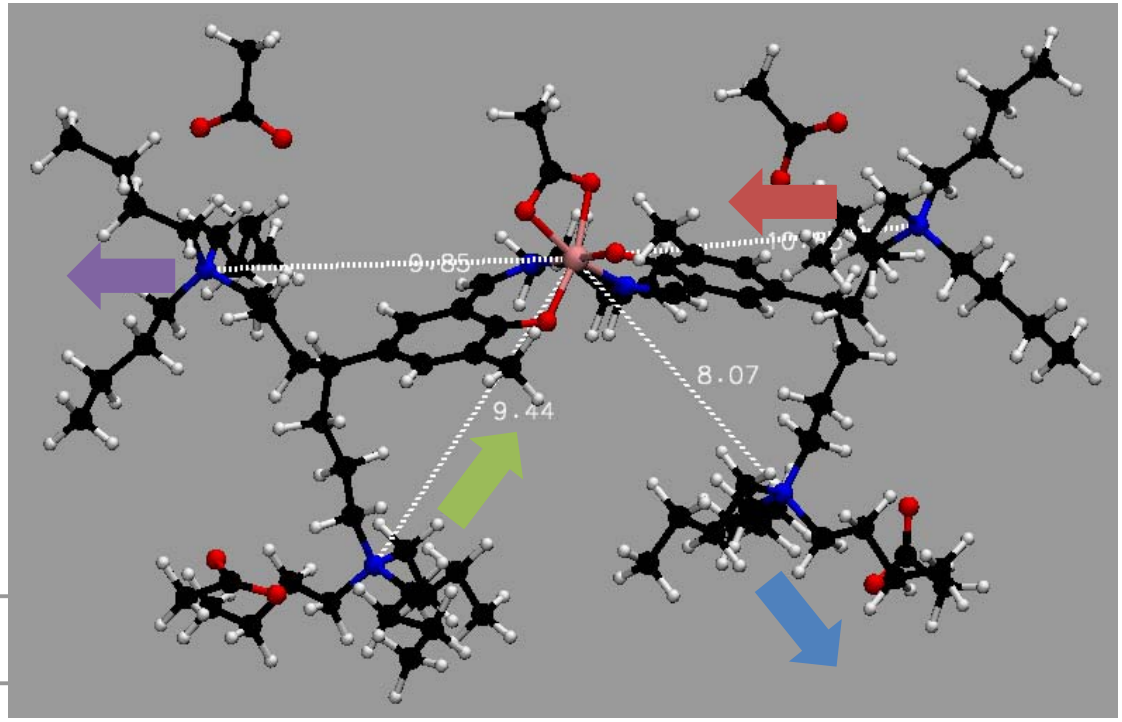
N-Co 9.44 A

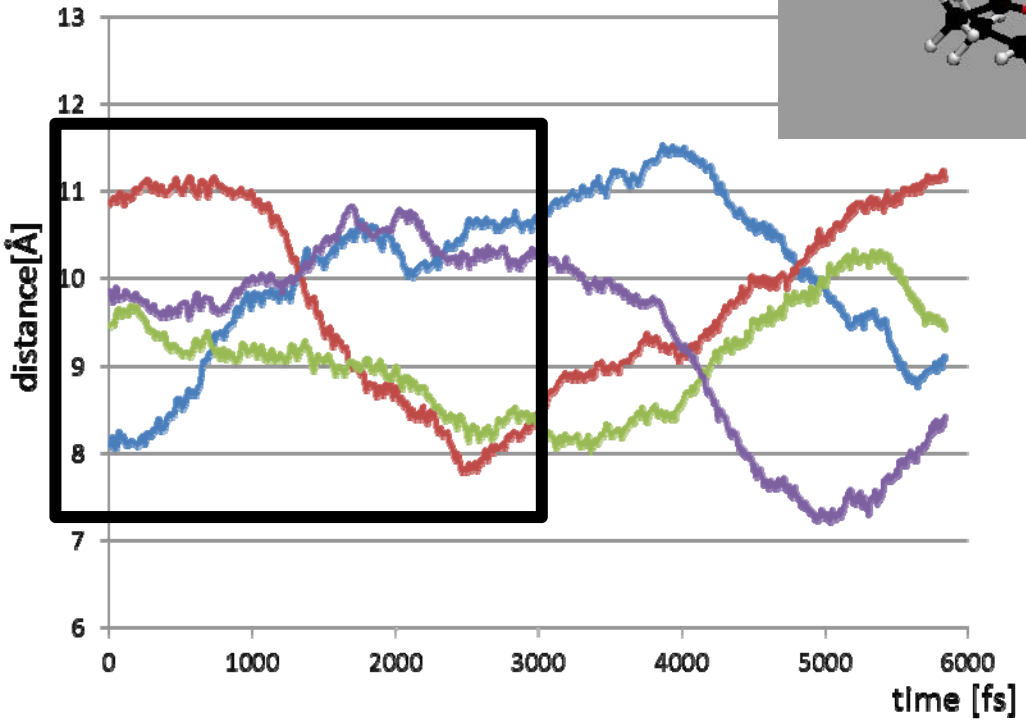
N-Co 10.95

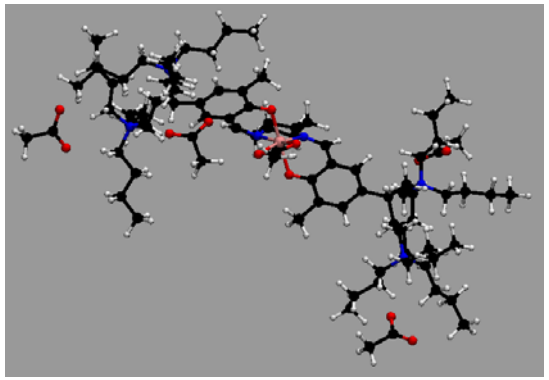
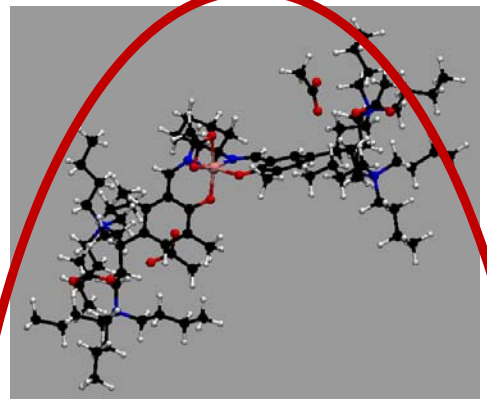
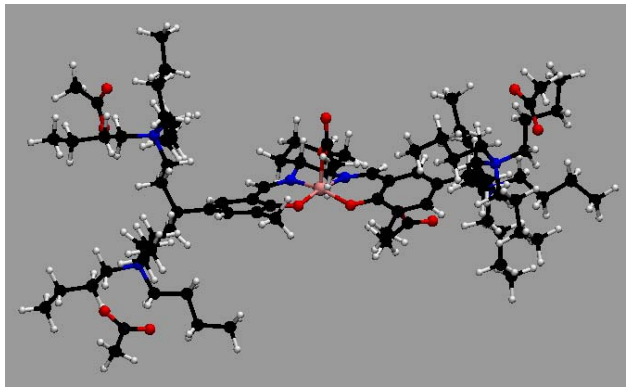
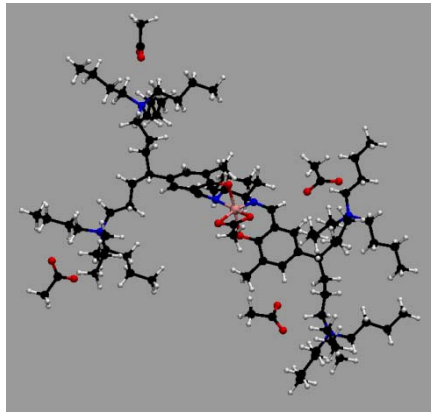
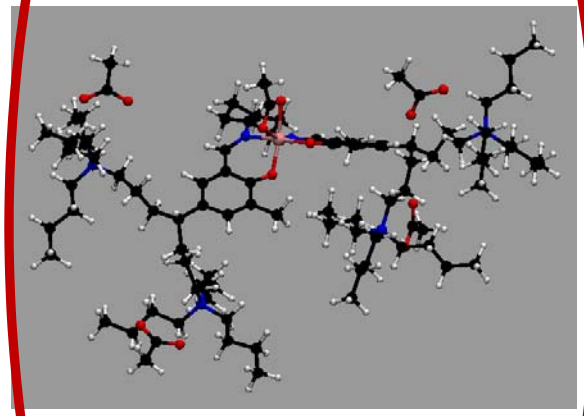
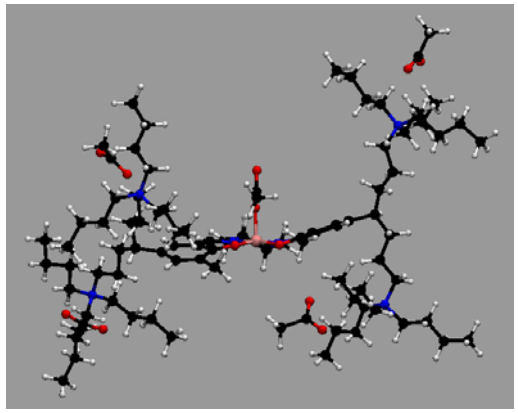
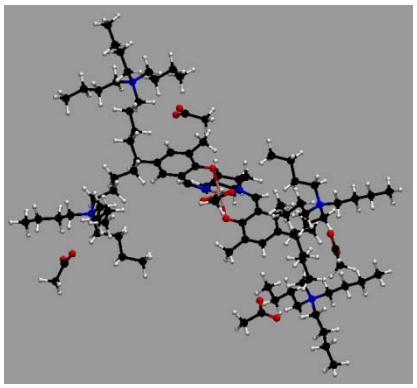
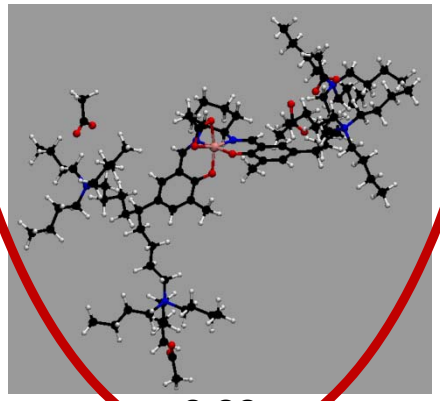
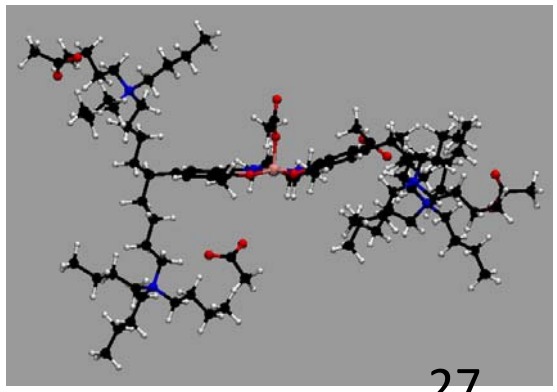
N-Co 8.07

Systems with four N^+-salts – DYNAMIC picture

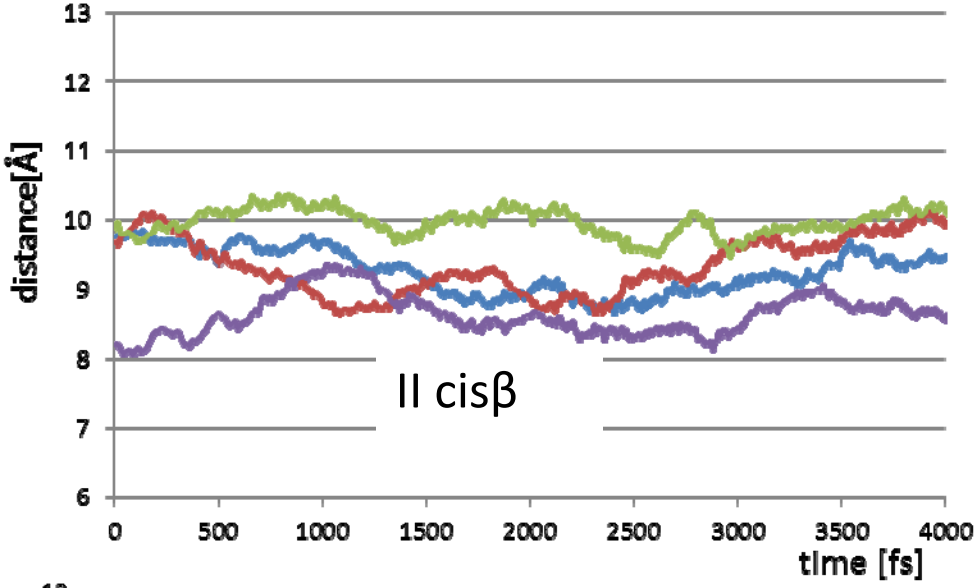
III cisβ

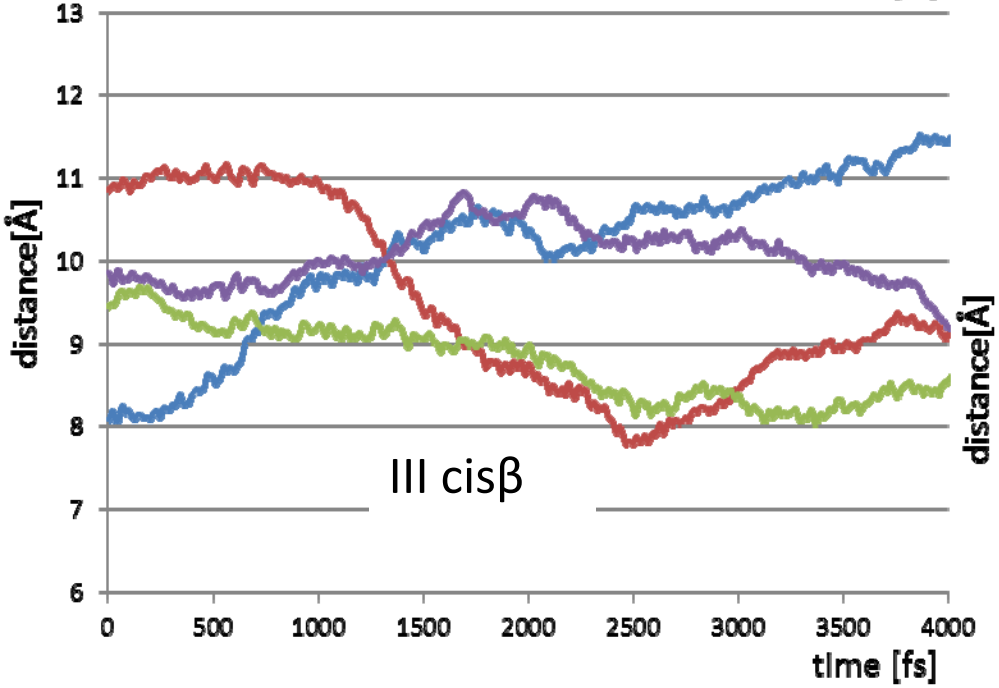


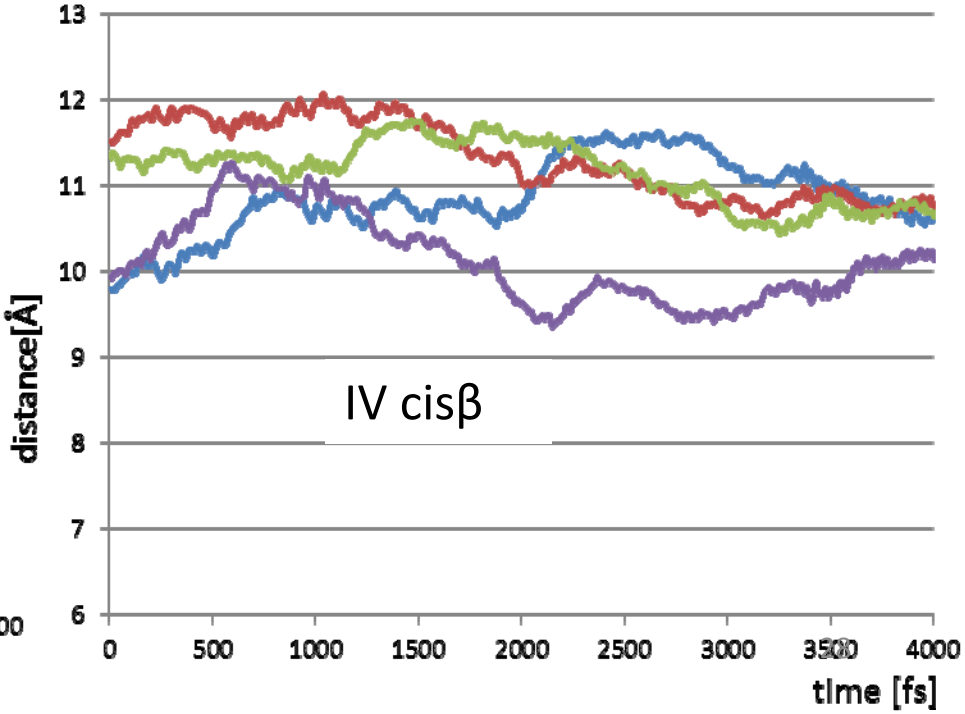


	cisα	cisβ	trans
II			
	21.96	0.00	11.08
III			
	32.38	0.00	10.74
IV			
	32.42	0.00	44.13

Systems with four N^+-salts – DYNAMIC picture







Summary & Future research

Summary

With the increase in chain length the preference of cisβ is stronger

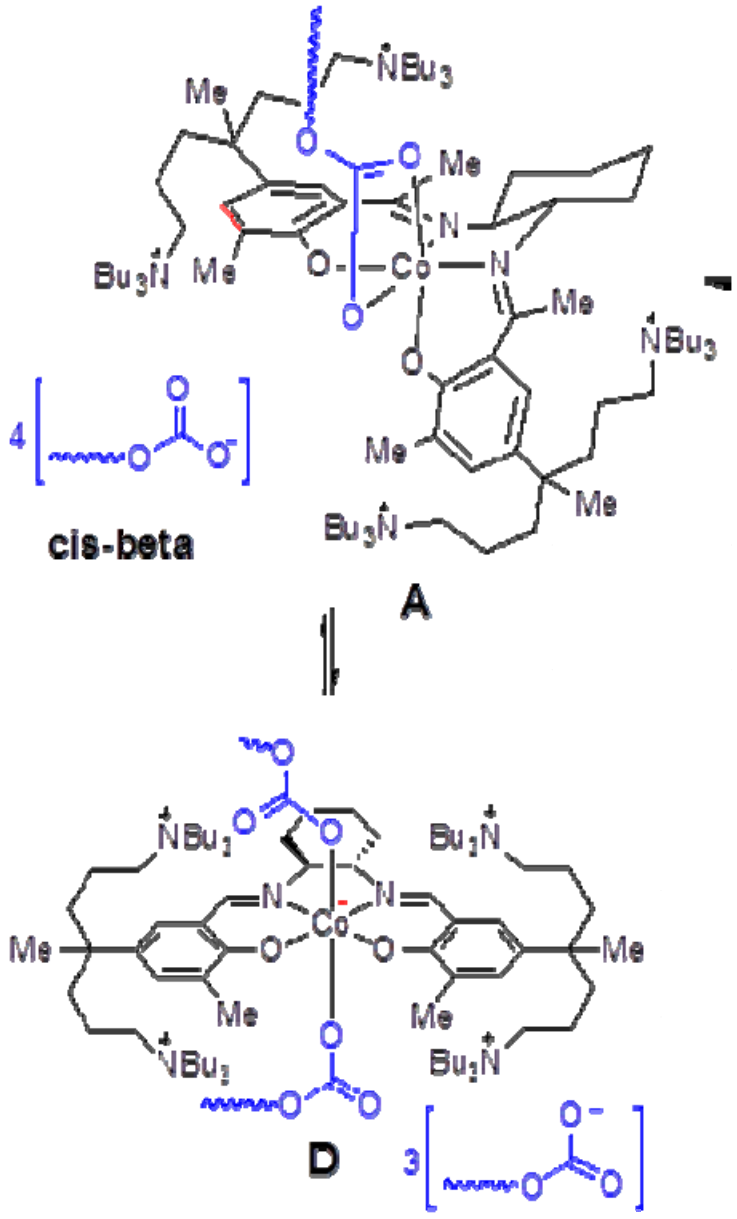
Chain movement is strongly affected by the chain-length

Future

bonding of co-monomers to metal center

investigation of elementary reactions in the copolymerization mechanism

Future research – mechanism of copolymerization



	trans	cisβ	cisα
	[kcal/mol]	[kcal/mol]	[kcal/mol]
II	11.08	0.00	21.96
III	10.74	0.00	32.38
IV	44.13	0.00	32.42

Acknowledgments