

## CONTROL IN TRANSITION METAL CATALYZED ORGANIC SYNTHESIS

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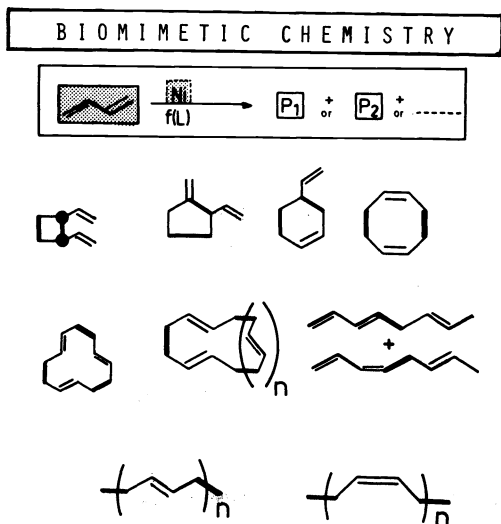
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**Abstract** - Transition metal catalyzed Organic Synthesis is an important strategy in synthetic chemistry. The wanted control in the reaction pathways to the target molecules in Organic Chemistry is normally achieved by functional group addition in the educts, followed by functional group interchange in the products. The more efficient way in Catalysis is to introduce the wanted order parameters into the process itself. Three strategies for the development of given catalytic systems are presented: (I) titration of the whole catalytic system, (II) system enlargement and (III) replacement of atoms in a given system. For the last two strategies four rules based on the inner structure of the Periodic System of Elements are proposed. A general model for "catalyst condition" supports these proposals.

Organic Chemistry of today tends more and more to "synthetic engineering". Simple, efficient synthetic methods of general application are required. The expansion of synthetic strategies in organic synthesis by the use of transition metals as modifiers made accessible new synthetic pathways (stoichiometric and catalytic) of general interest (Ref. 1). But by introducing transition metal complexes into synthesis one is faced with the fact that multiple competing reaction pathways have to be controlled. Slight changes of the preparative conditions can

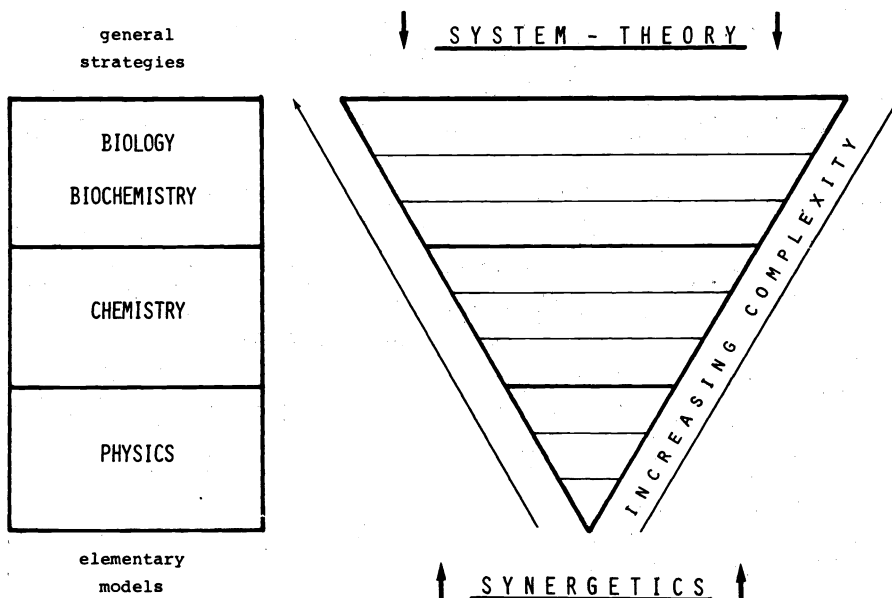
have a dramatic effect on the resulting selectivity. This is especially true for catalytic systems. By starting e.g. from the educt butadiene and even the same metal "Nickel" a wide range of products in high selectivity is available by changing the ligand field of the metal (Ref. 2) (by adding or removing various amounts of different types of bases and acids or even electrons or protons): SCHEME 1 (Ref. 3-6). Nature applies the same strategy starting e.g. from "active acetic acid". She produces a great variety of natural products by only changing the process determining enzymes (metal-catalysis as biomimetic chemistry (Ref. 7)).

SCHEME 1



Therefore simple rules and strategies are needed, which help to control and optimize the transition metal catalyzed organic syntheses. This leads to general questions like: What are the basic conditions for order to appear? What information determines the selforganisation of a system? What are the basic order parameters? - fundamental questions in chemistry as well as in the neighbouring disciplines Physics and Biology. As superposed ideas Synergetics (Ref. 8) and System-Theory (Ref. 9) have made valuable contributions to the method of investigation in systems of high complexity as well as to their understanding. Chemistry being the mediator between these fields of increasing complexity can be a leader in elucidating the basic principles on a molecular level (SCHEME 2). With respect to this, transition metal catalysis can play a key role.

SCHEME 2



In this lecture we want to demonstrate three fundamental strategies for varying the information of a catalytic system, thereby systematically changing the order in structure and reactivity. SCHEME 3 shows the three strategies to optimize a given catalytic system: variation of the concentration of participating molecular species (Strategy I), system enlargement (Strategy II) and especially systematic replacement of atoms in the given molecules (Strategy III).

SCHEME 3

**QUESTION :** HOW CAN WE OPTIMIZE A CATALYTIC SYSTEM ?

**STRATEGIES**

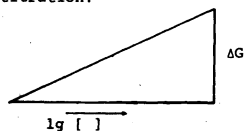
**I**

Variation of concentration

in a given system

e.g.

control by the amount of every individual species. Optimization by applying the method of inverse titration.



**II**

System enlargement

Variation of the number of participating species within multicomponent systems; control by the amount of individuals. Optimization by going from

e.g.

two component systems to three component systems to...

**III**

Replacement of atoms

Variation of atoms in a molecule, with a given constant pattern of connections.

e.g.

Optimization by systematic change of order parameters via atom replacement

APPLICATION OF THE HEURISTIC CONCEPT PSE - SR

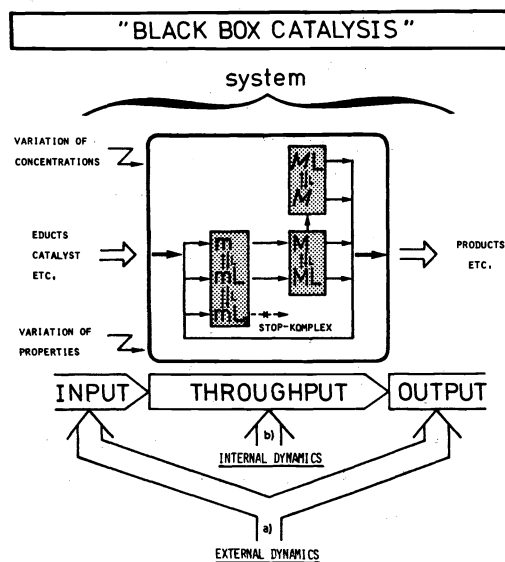
To systematize the decisions during investigation we used the following pragmatic procedure:

- I, Define the appropriate **S**YSTEM **M**ODEL **M**ETHOD of investigation
- II, Perform experimental variations of following kind **T**YPE **A**MOUNT **P**OSITION **S**YMMETRY

#### VARIATION OF CONCENTRATION (STRATEGY I)

In the analysis of the structure of a system with high complexity the way of thinking in "SYSTEM ANALYSIS" (Ref. 9) has organizing power. Accordingly the catalytic system is like a "black box" containing subsystems and therein elements: SCHEME 4. Because the internal dynamics of the THROUGHPUT is not generally open to a direct experimental observation (the concentration of the intermediates may be too low for direct spectroscopic investigation, but see Ref. 10) the method of choice is an INPUT/OUTPUT correlation. A variation of the initial conditions of the INPUT is related to a systematic change of the product distribution. This change of the dynamics in the overall system is examined by a "titration of the whole catalytic process" e.g. with controlling Lewis-bases (Ref. 11 and 12). For the three component system Ni(COD)<sub>2</sub>/diphenylphosphane/butadiene (1:X:170) the resulting ligand concentration control map is shown in SCHEME 5. As an effect of varying the chemical potential by varying the [L]<sub>0</sub>/[Ni]<sub>0</sub> ratio on a logarithmic scale several controlling ligand association processes are recognizable. To obtain information on how the controlling ligand associations are related to the individual subsystems of the catalytic system, partial control maps are deduced from the original one (degree of oligomerisation, distribution of the dimers or the trimers). A detailed analysis leads to a subsystem scheme, which gives an insight into the relationship of the different educt-, intermediate-, product- and inert stop-complexes and the possible number of stepwise, controlling ligand associations (Ref. 2). Furthermore an inspection of the ligand concentration control map shows the synthetic realisations and limitations of the given catalytic system. Three of the oligomers can be synthesized in high yields by only changing the metal to ligand ratio: ttt-cyclododecatriene ([L]<sub>0</sub>/[Ni]<sub>0</sub> < 10<sup>-2</sup>); cyclooctadiene ([L]<sub>0</sub>/[Ni]<sub>0</sub> ≈ 1) and 4-vinylcyclohexene ([L]<sub>0</sub>/[Ni]<sub>0</sub> ≈ 3).

SCHEME 4



Method of investigation ( one parameter variation ) :

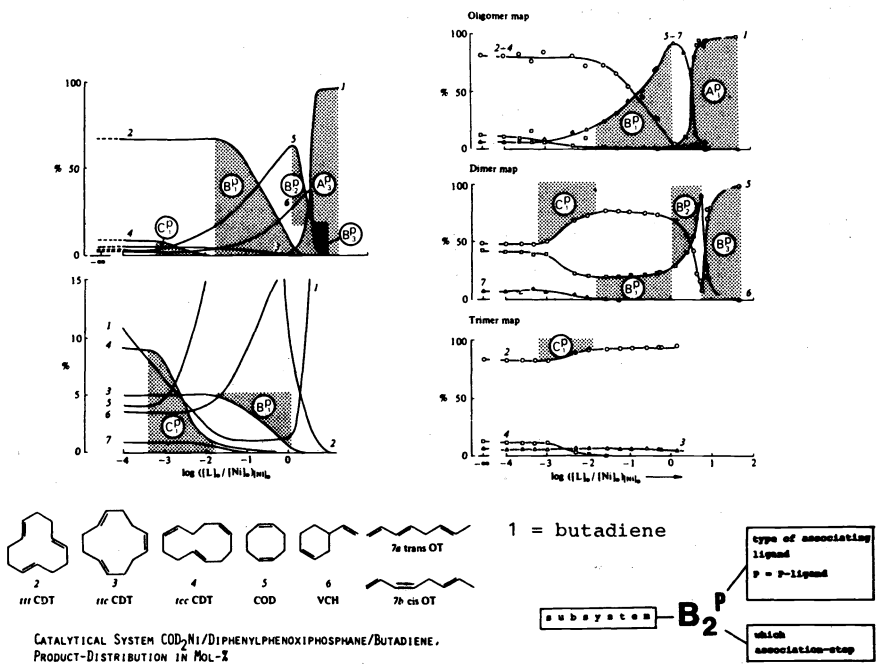
- INPUT/OUTPUT correlations ( educt/product correlations )
- Spectroscopic investigation of the THROUGHPUT

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**TITRATION OF A CATALYTIC SYSTEM : INPUT/OUTPUT CORRELATION**

SCHEME 5

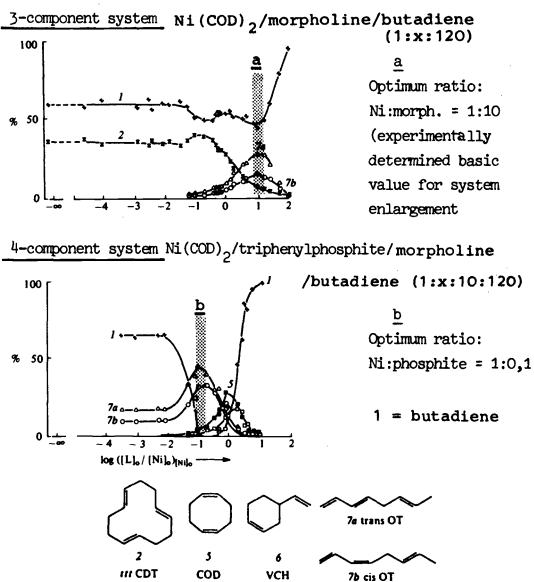


SYSTEM ENLARGEMENT (STRATEGY II)

In the three-component system  $\text{Ni}(\text{COD})_2/\text{sec. amine}/\text{butadiene}$  the oligomerisation of butadiene is shifted to the formation of acyclic octatrienes (7 a) and (7 b) (Ref. 13). For the secondary amine morpholine an  $[\text{amine}]_0/[\text{Ni}]_0$  ratio of 10 leads to the best selectivity: SCHEME 6.

SCHEME 6

**SYSTEM - ENLARGEMENT**



However, the catalytic efficiency is low; after a conversion of 30 % butadiene the catalytic activity ends because stop complexes are formed (reversibly). There is no way of further optimizing the catalytic system by variation of the concentration of the components. One possible further strategy is "system enlargement", a further carrier of order is included. Keeping the optimal ratio  $[\text{morpholine}]_0/[\text{Ni}]_0$  (= 10) constant, a fourth component (triphenylphosphite) is introduced into the system and again optimized via the "method of inverse titration" (Ref. 2 ). (We choose further ligands for system enlargement by applying PSE - SR, see below). At a ratio of  $\text{Ni}(\text{COD})_2/\text{morpholine}/\text{triphenylphosphite}$  = 1:10:0.1 a high cooperativity of the ligands is obtained, leading to the wanted octatrienes in high selectivity without stop complex formation. The strategy of system enlargement can prevent from stop complex formation (octatriene-synthesis:

$\text{Ni}(\text{COD})_2/\text{H-NR}_2$  /butadiene +  $\underline{\text{P}}$ -ligand: see later PSE - SR), can open new reaction channels (2:1 co-oligomerisation of butadiene and aldehyde;  $\text{Ni}(\text{COD})_2$ /butadiene/aldehyde + P-ligand: Ref. 14) and can switch the catalytic activity from one reaction channel towards another one ( $\text{Ni}(\text{COD})_2/\text{HNR}_2$ /butadiene: octatriene-synthesis; +  $\text{Al}(\text{OR})_3$ : synthesis of e.g. octadienylated amines: Ref. 15). For the role of two co-effectors in high and low concentration see Ref. 16, too.

#### ELEMENTARY PHYSICAL MODELS FOR THE ROLE OF BASIC ORDER PARAMETERS IN CATALYSIS

Both presented strategies do focus on the optimization of an ensemble of components by varying the concentrations of the given partners (Strategy I) or the additional compound after system enlargement (Strategy II). A third strategy can be a systematic variation of the synergic interaction of the components (molecules (Strategy II) or even atoms (strategy III) within the molecules). The course of a chemical reaction is characterized by a passage through several energy states. The essential catalytic interaction may be seen as a unique particle, the unified substrates and the catalyst coupled at the transition state with the highest activation energy (see Ref. 17), nearly comparable with the coupling of two electric circuits: SCHEME 7. The mechanical analogon is a coupled sympathetic pendulum (demonstration). The energy change as a result of the oscillatory situation during catalysis depends on the symmetry in the coupling (A or S; for simplifying to A/S in structure and process see Ref. 18) of the components. The catalytic interaction relation is performable by a simple quantum mechanical procedure with a system of two simultaneous SCHROEDINGER equations (Table 1). The solution of this system leads to a typical resonance relation as a "catalyst condition". The

SCHEME 7

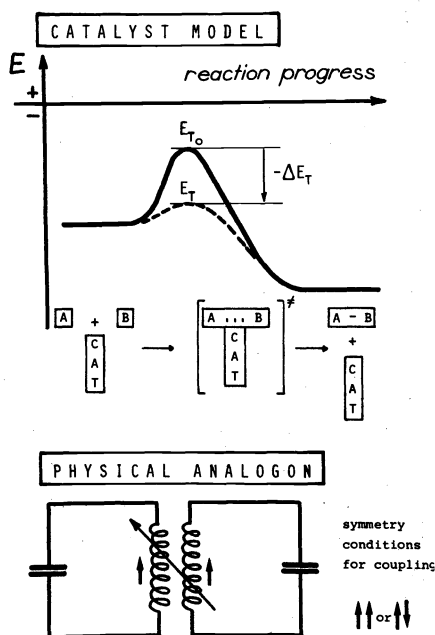


TABLE 1

Mathematical equations for the catalytic model system

**SIMULTANEOUS SCHROEDINGER EQUATIONS**

$$\frac{\hbar^2}{2m} \cdot \Psi_T'' + (E - V_T) \cdot \Psi_T = \bar{V}_1 \cdot \Psi_C$$

$$\frac{\hbar^2}{2m} \cdot \Psi_C'' + (E - V_C) \cdot \Psi_C = \bar{V}_1 \cdot \Psi_T$$

**ENERGY EIGENVALUES FOR THE COUPLED SYSTEM**

$$E = \frac{1}{2} \cdot (E_{T_0} + E_{C_0}) \pm \frac{1}{2} \cdot (E_{C_0} - E_{T_0}) \cdot \sqrt{1 + 4 \cdot \frac{\bar{V}_1^2}{(E_{C_0} - E_{T_0})^2}}$$

$$E \equiv E_T \quad E_T - E_{T_0} = \Delta E_T$$

**RESONANCE RELATION AS A CATALYST CONDITION**

$$\Delta E_{T_{1,2}} = \frac{1}{2} \cdot (E_{C_0} - E_{T_0}) \cdot \left[ 1 \pm \sqrt{1 + 4 \cdot \frac{\bar{V}_1^2}{(E_{C_0} - E_{T_0})^2}} \right]$$

$$\Delta E_{T_1} \approx - \frac{\bar{V}_1^2}{E_{C_0} - E_{T_0}}$$

$$\Delta E_{T_2} \approx (E_{C_0} - E_{T_0}) + \frac{\bar{V}_1^2}{E_{C_0} - E_{T_0}}$$

**SYMMETRY CONDITION**

$$\Delta E_T = \bar{V}_1 \cdot \frac{\Psi_C}{\Psi_T}$$

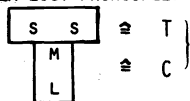
decrease of the activation threshold - being the most important parameter for a theoretical determination of catalytic phenomenon at all - results as a function of the eigenvalues of transition state of the unified organic moieties ( $T_0$ ), of the catalyst ( $C_0$ ), the interaction energy ( $\bar{V}_1$ ) and its symmetry ( $\uparrow\uparrow=\sigma$  or  $\uparrow\uparrow=C_2$ ). The catalyst condition clarifies especially that activation (catalysis) and inhibition effects are only expectable for small differences between the eigenvalues of transition state and catalyst - this is manifesting the selectivity performance of catalytic behaviour. The resonance condition in relation to the energy and symmetry condition of the system in resonance is presented in SCHEME 8. Regarding a symmetric (antisymmetric) coupling catalysis or activation will occur only if the catalyst eigenvalue is situated above (below) the transition state. By changing the symmetry of the fragment coupling a catalyst is transformed into an inhibitor and vice versa.

RESONANCE CONDITION IN COUPLED SYSTEMS OF SIMILAR ENERGY

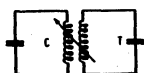
SCHEME 8

EXPERIMENTAL	SYMMETRY RESTRICTION OF COUPLING	"C"		"C <sub>2</sub> "	
		← →		→ →	
VARIABLES	ENERGY RELATION OF THE SYSTEMS IN RESONANCE	$E_{C_0} < E_{T_0}$	$E_{C_0} > E_{T_0}$	$E_{C_0} < E_{T_0}$	$E_{C_0} > E_{T_0}$
RESULTING EFFECT	ENERGY CHANGE OF THE COUPLED SYSTEMS	$\Delta E_T < 0$ catalyst	$\Delta E_T > 0$ inhibitor	$\Delta E_T > 0$ inhibitor	$\Delta E_T < 0$ catalyst

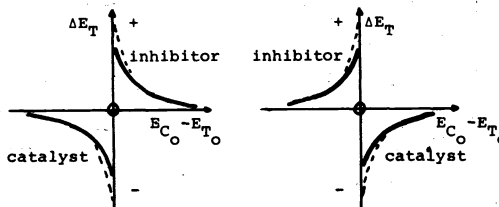
CHEMICAL ANALOGON:  
(METALA-LOGY PRINCIPLE)



ELECTRICAL ANALOGON:  
COUPLED ELECTRIC CIRCUITS



SYMPATHETIC PENDULUM



The sympathetic pendulum has a positive coupling energy. The chemical analogon has a negative coupling energy for bonding interaction, leading to inverse symmetry behaviour.

In a catalytic system containing several different intermediate complexes, every resonance condition between the transition metal "trunk complex" (see Ref.19) and the unified organic moieties has to be optimized in its energy relation and symmetry condition. The experimental strategies for this are summarized in SCHEME 9. The Metala-logy Principle (for application see Ref. 2) divides the important intermediate transition metal complexes in analogy to the above mentioned theory of catalysis into two molecular fragments the unified organic moieties and the catalyst "trunk complex" (for the different types of perturbation see PSE - SR below).

EXPERIMENTAL PROOF FOR THE ROLE OF SYMMETRY IN FRAGMENT COUPLING

An excellent proof for the role of symmetry in fragment coupling of a catalytic system is

SCHEME 9

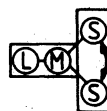
### METAL - LOGY-PRINCIPLE: Experimental Strategy

(S) : SUBSTRATES TO BE COUPLED

(M) : COUPLING METAL

(L) : MODIFYING LIGAND

\* by TYPE  
A MOUNT  
P OSITION  
S YMMETRY



* $\hat{=}$ Perturbation	at the System	in the System	Case
Substrate (S)			I
Coupler (L)-(M)			II

given in SCHEME 10. Change of the symmetry of the FMO's of the controlling ligand (even/odd numbers of electron pairs of the  $\Pi$ -system) (Ref. 20) has the expected effect on the catalytic activity and thereby reverses the selectivity of the competing reaction pathways.

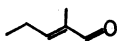
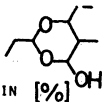
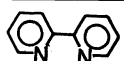
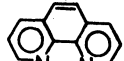
Another way of examining strategies for changing symmetry in fragment coupling is an investigation into the intensities of symmetric and antisymmetric coupled molecular vibrations in

SCHEME 10

### CHANGING SYMMETRY IN FRAGMENT COUPLING

S YSTEM : Ni / N N / PROPANAL  
M ODEL : FMO - THEORY  
M ETHOD : GC - ANALYSIS  
of  
investigation

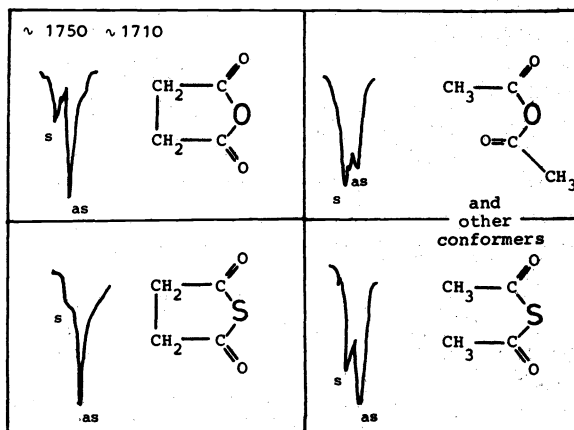
BY T YPE : EVEN/ODD ELECTRON PAIRS  
A MOUNT : Ni / N N / PROPANAL = 1:10:1000  
P OSITION : LIGAND  
S YMMETRY : A / S IN FMO'S

	CONVERSION		 YIELD IN [%]
 HO(A) LU(S)	LOW	17	82
 HO(S) LU(A)	HIGH	94	5

## EFFECTS OF ORDER PARAMETERS ON S/AS-COUPLING OF MOLECULAR VIBRATIONS

SCHEME 11

SYSTEM:	anhydrides	TYPE :	DO/ACC; cyclic/open		
	MODEL :		FMO-THEORY; PSE - SR (AII/AIV)	AMOUNT :	one heteroatom O/S
	METHOD:		IR		POSITION :
of investigation		SYMMETRY :	-		



For the given system:

- O favours s-coupling
- S favours as-coupling
- cycl. favours as-coupling
- open favours s-coupling

	cycl. <sub>as</sub>	open <sub>s</sub>
O <sub>s</sub>	as	s
S <sub>as</sub>	as	as

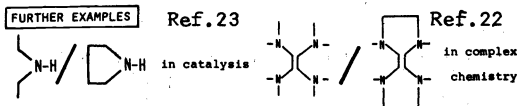
IR-spectroscopy. This is demonstrated for anhydrides in SCHEME 11. Changing from cyclic to open structure reverses the intensities of the symmetric and antisymmetric coupled vibrations of the carbonyl-groups as well as changing the DONOR / ACCEPtor-quality of the coupling atoms (O / S). Having in mind that molecular vibrations can be regarded as initial perturbations

SCHEME 12

## CONTROLLING FACTOR CYCLIC/OPEN

REACTING SYSTEM	PRODUCTS yield in [%]	SELECTIVITY in [%]	
 Ref. 21a	1,4-add <sup>n</sup> 75/75 1,2-add <sup>n</sup>	82 18	40 60
 Ref. 21b	α-attack 83/81 γ-attack	95 5	3 97
 Ref. 21c		100 0	"transfer of methyl and vinyl groups to the β-carbon atom occurs"
 Ref. 21d		0 (3h) → 100 (10 min)	

## FURTHER EXAMPLES

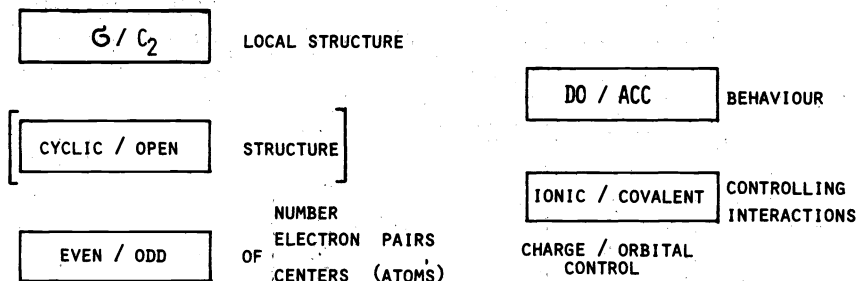


towards intramolecular reaction channels it is no more surprising that changing the structure of a complexing solvent from open to cyclic (e.g. diethylether vers. THF) can be another way for realizing the expected reversal of ordering influences in chemical reactions (SCHEME 12) (Ref. 21). The general nature of this influence can be further demonstrated by examples from the field of transition metal complexes (Ref. 22) and catalysis (Ref. 23). The most favorable position of nucleophilic attack on 18 electron organo transition metal cations containing unsaturated hydrocarbon ligands can be predicted by taking into consideration the order parameters open / cyclic and even / odd carbon centers of the  $\Pi$ -system (Ref. 24). More order parameters for changing the symmetry of fragment coupling are summarized in SCHEME 13. A change in one of these parameters may correspond to a characteristic change in molecular structure as well as thermodynamic resp. kinetic selectivity.



SCHEME 13

## BASIC ORDER PARAMETERS IN MOLECULAR INDIVIDUALS



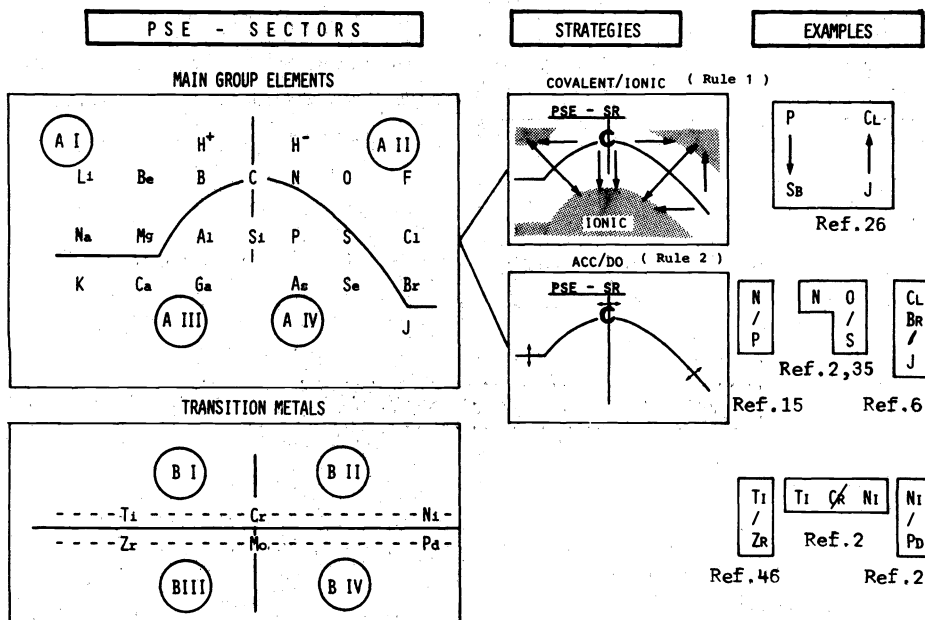
resulting in change of fragment coupling (s/as) leading to changes

in { thermodynamic selectivity: stabilisation / destabilisation:  $\Delta\Delta G_0$   
 kinetic selectivity: activation / inhibition :  $\Delta\Delta G^\ddagger$

## REPLACEMENT OF ATOMS (STRATEGY II)

As shown for IR-frequencies above, a replacement of atoms with changing the DO / ACC-quality at this center may have a characteristic effect on the order of the given molecular system. This strategy of systematic replacement of atoms for changing order parameters can be expanded to a heuristic principle. The periodic system of the main group elements as well as the transition elements can each be divided in four sectors (Ref. 9). The exact positions of the borderlines depend on the organic moiety under investigation. For carbon II-systems the positions are exemplified in SCHEME 14 (left side). Each sector of chemical elements is character-

SCHEME 14



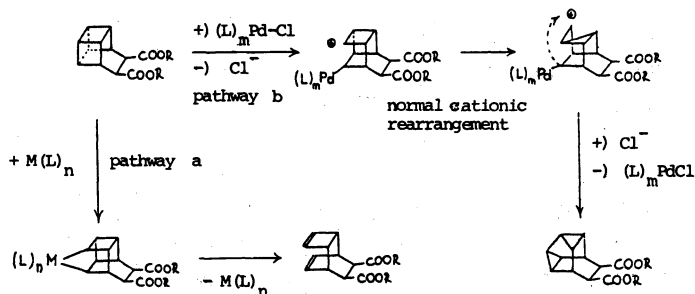
ized by a certain ordering influence. Therefore an atom replacement by crossing the borderline may have characteristic effects on the order of the given system (Ref. 25). We should like to present four Periodic System of Elements (PSE) - Sector Rules:

PSE - Sector Rule 1:

Substitution of an atom near the borderline by another one from far away (dotted area in

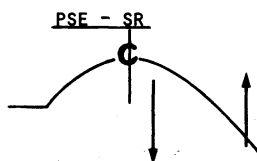
SCHEME 15

EXAMPLE FOR PSE - SR1



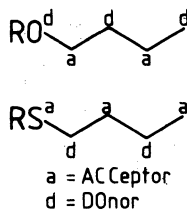
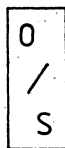
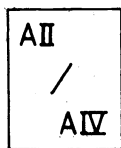
Ref. 26

PdX <sub>2</sub> (YH <sub>3</sub> ) <sub>2</sub> pathway a / pathway b	Y=			
	Sb	As	P	
X=	Cl	9/100	38/62	59/41
J	77/23	94/6	98/2	

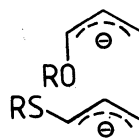


PSE - Sector Rule 2:

Eventhough the type of directing influence does not change during "atom replacement" (see PSE - SR 1) a substitution of atoms from different sectors by one another may alternate the corresponding reaction pattern (changing DOnor / ACceptor-quality at a given position) and simultaneously the local symmetry in structure and/or process. The molecular graph should remain unchanged applying the "atom replacement", i.e. no structural isomerism should be introduced. But as a result of this substitution molecular order parameters may change and characteristically affect the stereochemistry of the molecular system. This can easily be demonstrated in Organic Chemistry by e.g. changing Oxygen versus Sulphur (Sector A II versus A IV):



reactivity  
pattern (Ref.27)

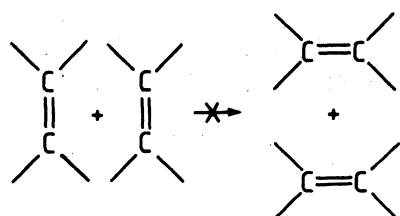


stereochemistry  
(Ref.28)

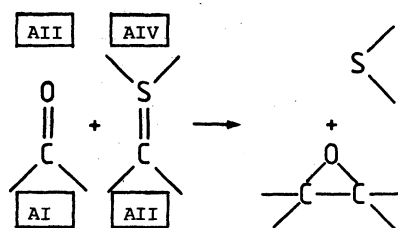
SCHEME 14 right upper part) may change the directing molecular interaction from covalent (orbital control) to ionic (charge control). For example the rearrangement of the 1,1-bishomocubanderivative (Ref. 26) in SCHEME 15 is orbital controlled using PdJ<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as a catalyst. The reaction pathway switches from orbital control (pathway a) towards a normal cationic rearrangement, after Iodine is replaced by Chlorine and Phosphorus by Antimony within the catalyst species.

An atom replacement between atoms from sector A II by A IV can reverse the reactivity pattern, a common preparative strategy in Organic Chemistry (Umpolung) (Ref. 29). But if one does not bear in mind the inner connexions between DO / ACC - behaviour and other order parameters (see SCHEME 13), "stereochemistry shows its ugly head" (Ref. cit. in Ref. 27).

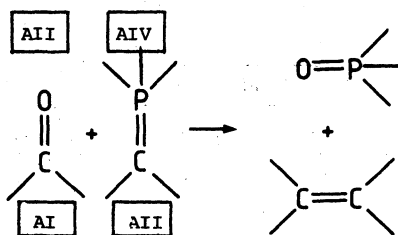
Another famous example for "atom replacement" is the so called Wittig reaction (Ref. 30). The replacement of  $sp_2$ -hybridized Carbon by Oxygen (A II) and Phosphorus (A IV) introduces the reversal reactivity pattern into two "olefines" and thereby makes the uncatalysed meta-thesis-reaction possible.



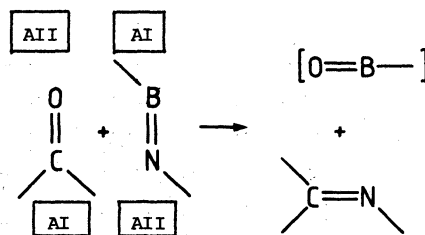
Metathesis reaction (uncatalyzed)



"Thia-Wittig" reaction (Ref.31)



Wittig reaction (Ref.30)



"Bora-Wittig" reaction (Ref.32)

SCHEME 16

### CATALYTIC OLIGOMERISATION OF PROPANAL

		SUBSTRATE	YIELD IN [%]	
CATALYSTS				
a)		$\text{Na}_2\text{CO}_3$	100	0
		HCl	56	42
b)		$\text{Ni} \cdot \text{C}_2\text{O}_4$	100	0
		$\text{Na}_2 \text{Pd Cl}_4$	2	97
c)		$\text{Ni} \cdot \text{C}_2\text{O}_4$ (with ligand)	100 (100)	0 (0)
		$\text{Ni} \cdot \text{C}_2\text{O}_4$ (with ligand)	34	66

a) protonation/deprotonation leads to  $c^+/c^-$  (in addition the controlling influence of the aldehyde/enol equilibrium has to be considered)





b) ligand field constant

c) metal constant

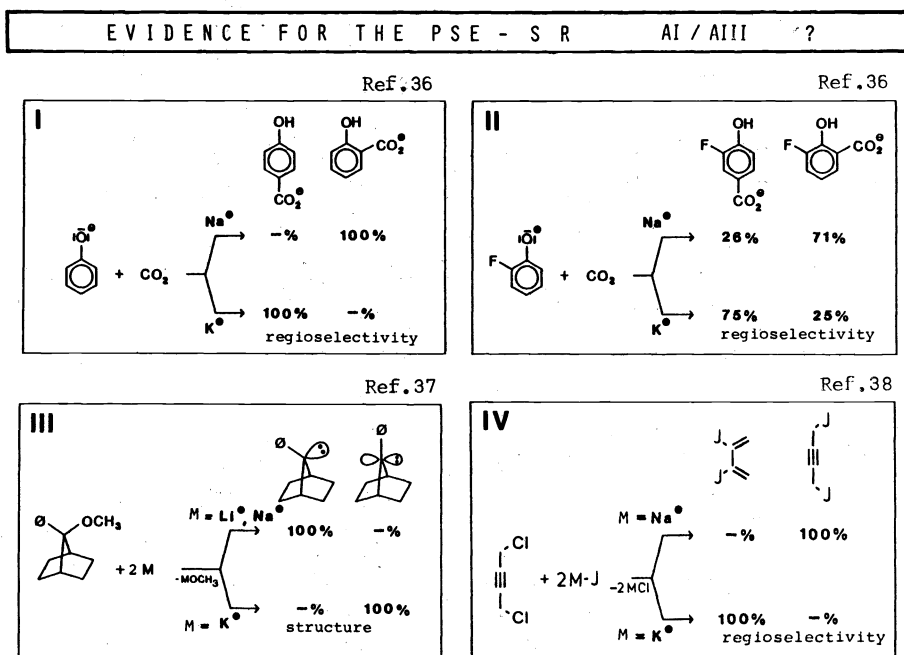
d) only existent at very low temperature

An example for the application of PSE-sector rule 2 in catalysis is shown in SCHEME 16. In particular the correspondence of atom replacement between sectors A I / A II, A II / A IV and B II / B IV is demonstrated (Ref. 20 a). The resulting selectivity shows the superiority of transition metal catalysis over acid / base catalysis in classical Carbonyl chemistry. More examples for atom replacement sector A II / A IV in catalysis are seen in SCHEME 17 (Ref. 33-35). The interconnectedness of the order parameters DO / ACC,  $\sigma / C_2$  and cyclic / open (see SCHEME 13) can be seen, too. In SCHEME 18 four examples are collected for atom replacement between sector A I and A III (Ref. 36-38). Even this strategy may lead to characteristic changes in structure and regioselectivity. Nevertheless the reason for this order control is not totally understood. Arguments regarding charge and partial covalence are still equally favoured.

SCHEME 17

EXAMPLES FOR HETEROATOM REPLACEMENT AII/AIV IN TRANSITION METAL CHEMISTRY			ORDER PARAMETERS OF THE PRODUCTS					
AII/AIV	SYSTEM UNDER INVESTIGATION	EFFECTS						
		REACT. RATE	CIS-1,4- / TRANS-1,4- / 1,2-PB [%]					
CL BR / J	Ni(COD) <sub>2</sub> /BUTADIENE/H-X : 1:250:1 Ref. 33	H-Cl	HIGH	84	13	3	TRANS / CIS	G / C <sub>2</sub>
		H-Br	LOW	72	25	3		
		H-J	HIGH	-	100	-		
N / P	Ni(COD) <sub>2</sub> /BUTADIENE/TPP 1:170:0.1 Ref. 34	10 H N (φ)ME	HIGH	75% N-OCTA-1,3,6-TRIENES			OPEN / CYCL.	
		10 H P (φ)ME	LOW	95% CYCLIC DIMERS				
O / S	Ref. 2,35 THERMOLYSIS OF PENTADI- ENYL-Ni-XCH <sub>3</sub> (DIMERIC)	-OCH <sub>3</sub>	LOW	 BYPROD. [%]			TRANS / CIS	G / C <sub>2</sub>
		-SCH <sub>3</sub>	HIGH	55%	20%	20%		
			THERMAL STABILITY					
				15%	35%	50%		

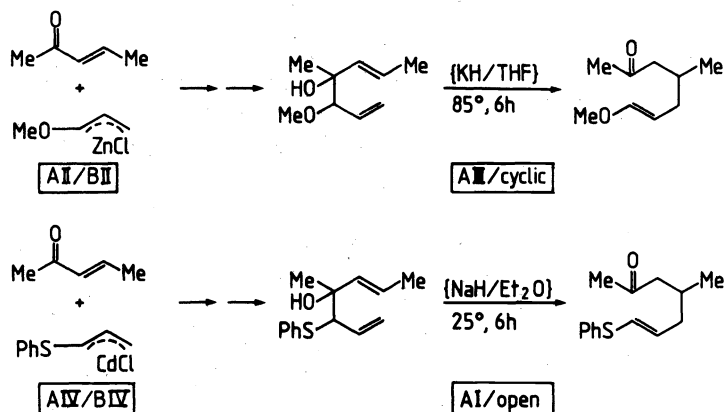
SCHEME 18



## PSE - Sector Rule 3:

One atom replacement following PSE - Sector Rule 2 may change order parameters in chemical reactions under the support of transition metal complexes, but the reaction conditions mostly have to be optimized anew. For optimizing symmetry and energy of fragment coupling (with reference to the "catalyst condition" SCHEME 8) the coupling of the fragments has to be readjusted. In many cases a second atom replacement can counterbalance the situation. Alternatively one can follow other strategies from SCHEME 13: This will restore the parent state of high selectivity and high reactivity after having successfully changed order parameters in the product spectrum through atom replacement via PSE - Sector Rule 2. E.g. alkoxydienoles

can be synthesized via a highly regioselective 1,2-dicarbonyladdition of alkoxyallyl Zn-Cl to enones. Such alkoxydienoles serve as viable precursors to monoprotected 1,6-dicarbonyl derivatives via an Oxa Cope rearrangement. However, the analogous Thia Cope rearrangement generally takes place under far milder conditions. Therefore this synthesis has to be varied after atom replacement of Oxygen by Sulfur (A II / A IV) in the alkoxyallyl-moiety. To optimize the reaction conditions the introduced order change has to be carefully counterbalanced by substituting Zinc by Cadmium (B II / B IV) and KH by NaH (A III / A I). Even the order parameter represented by the solvent (cyclic / open) was changed (Ref. 39).

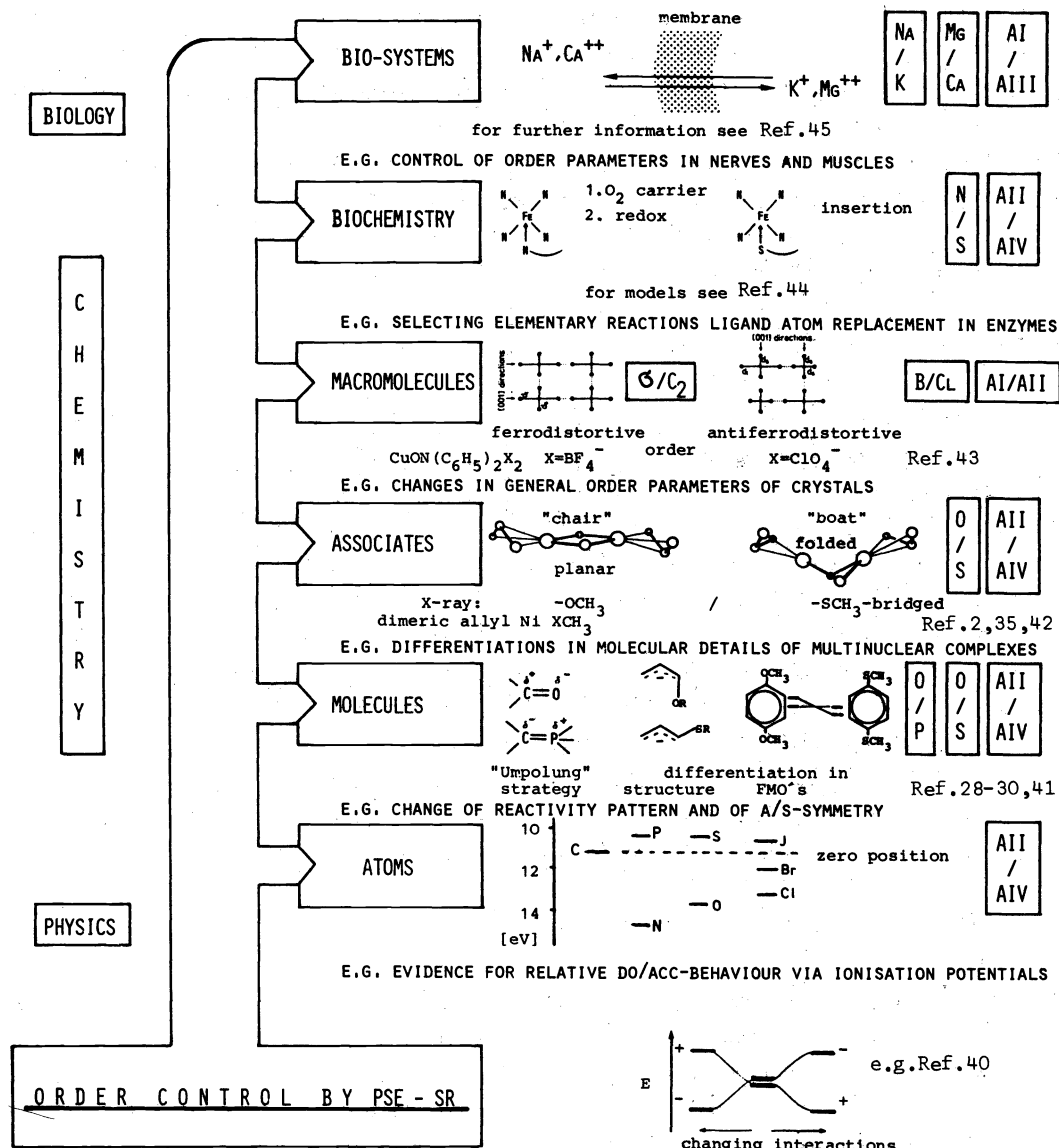


PSE - Sector Rule 4:

Multistep atom replacement may not necessarily be a strategy to adjust a given order (PSE - SR 3). In contrast this strategy can be used to systematically introduce disorder into a system. This is true for order control in general. It was e.g. demonstrated by SCHEME 10, that changing the symmetry of the FMO's of the controlling ligand (even / odd numbers of electron pairs of the  $\Pi$ -system) reverses the selectivity and affects the activity of the presented catalytic system. Interestingly a 1:1-mixture of both ligands suppresses the catalytic activity dramatically over the whole  $[L]_0/[Ni]_0$  range from  $10^{-3}$  to  $10^2$  (Ref. 20 a).

As it was demonstrated by several examples order control is of great importance for a realization of optimal synthetic pathways in Organometallic Chemistry. The authors assume that the presented concepts (especially the PSE - Sector Rules) can be easily expanded to other fields of chemistry (SCHEME 19).

Following synergetics (Ref. 8) the spontaneous formation of well organized structures is determined by the number of participating individuals or by introducing energy or mass into the system. Chemistry can contribute one more principle being significant for processes of self-organisation: The systematic change in the character of individuals, in chemistry the properties of the molecules respectively those of the atoms within the molecules. The corresponding rules may be derivable from the inner structure of the Periodic System of Elements.



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