MODERN ORGANIC CHEMISTRY: HOW IT WORKS

MIKHAIL S. NECHAEV, PH. D., D. SC.

MSU, TIPS RAS

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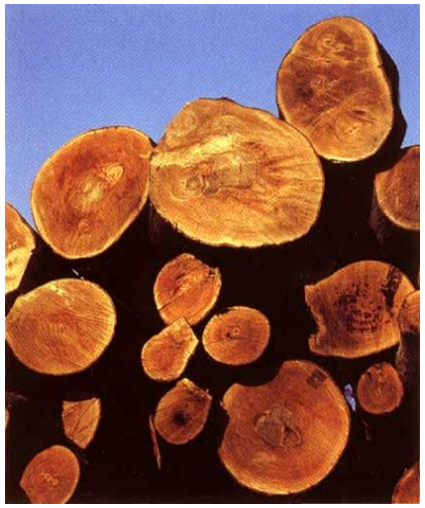
Outline

- What is modern organic chemistry
- Research in our group
- Applied research
- Concluding remarks

Modern organic chemistry

Life is organic …

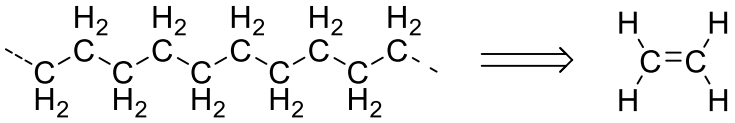


Evolution of technology, biomimetic approach

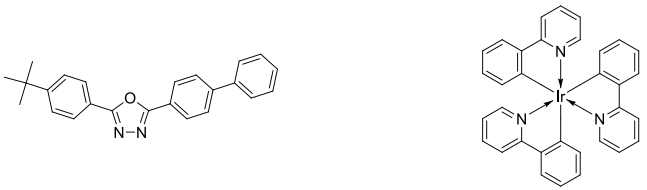
- Utilization of organic materials
- Approaches based on biological principles
- Artificial life

Levels of complexity

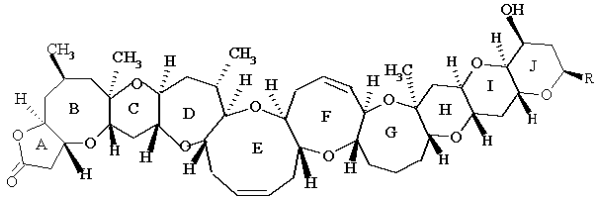
Polymers



Organic electronics



Drugs



If you want to make something new…
most probably, it will be organic!

What is organic chemistry?

Organic chemistry – chemistry of carbon containing compounds…

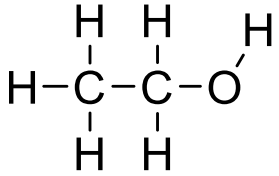
1828 – 1886

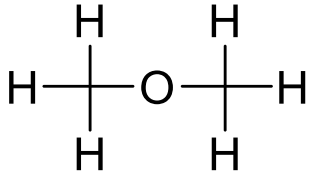
Alexander Mikhailovich Butlerov (1859):

«chemical nature of complex body is determined by nature of elemental parts, their quantity and chemical structure».

Structure of the molecule defines its properties.

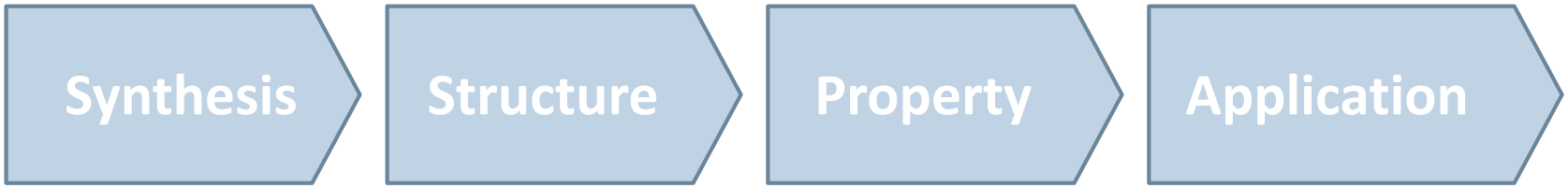
C_2H_6O





What is organic chemistry?

Research process in organic chemistry in 19th and 20th centuries



Chemists synthesized, studied and utilized MOLECULES

What is organic chemistry?

Nobody needs molecules!..

… but, everybody need molecular properties!

Drugs

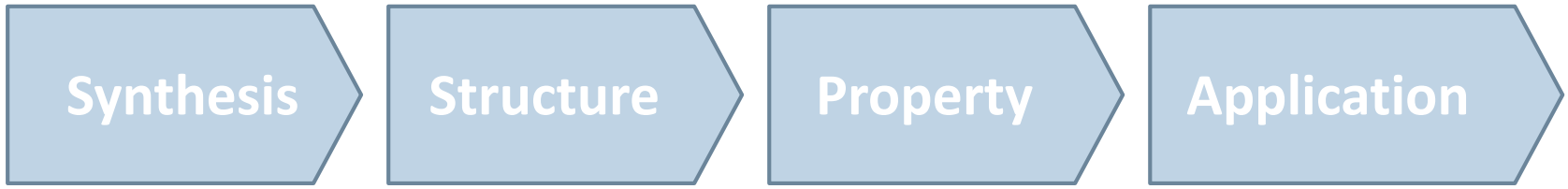
Interested

- Action
- Safety
- Price

NOT interested

- Chemical structure
- Formulation
- Polymorphism

What is organic chemistry?

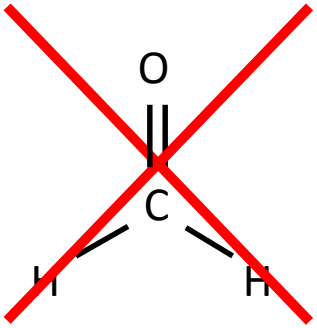


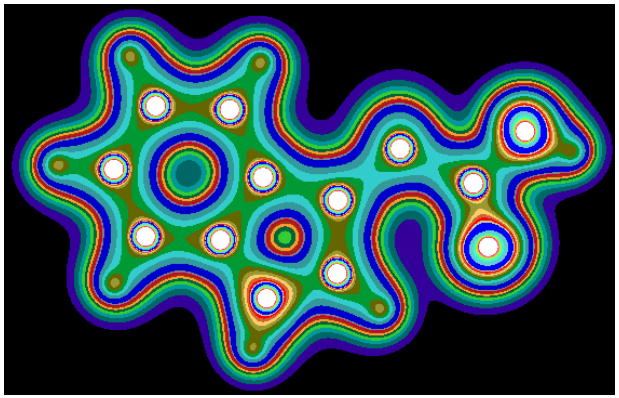
Organic chemistry – a science about how to make substances or materials with the needed properties based on carbon and other elements compounds.

Property → structure

Design and modeling of molecules

Quantum chemistry is a modern language



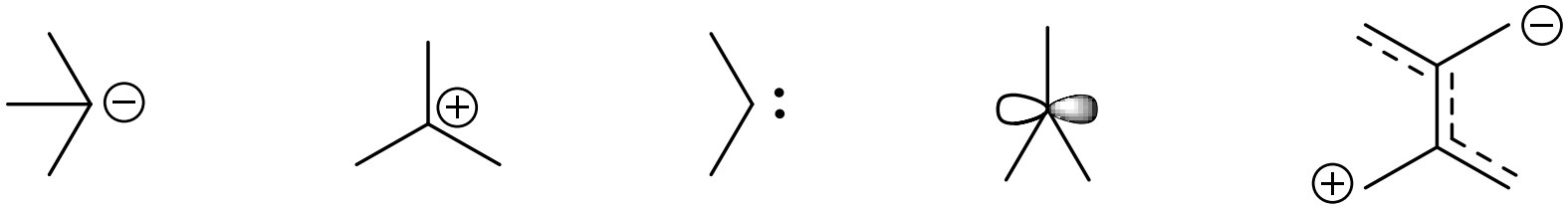


More advanced language enables us to describe and understand more complex problems

Structure → Synthesis

Experimental studies of reactive species

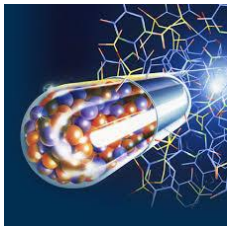
actio (lat.) – movement, action

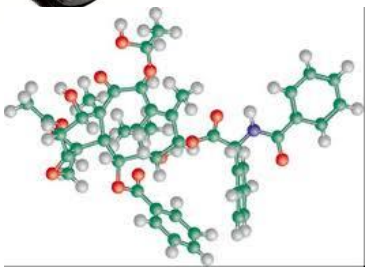


Synthesis → Application

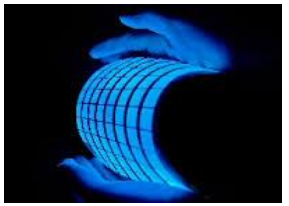
Catalysts

Drugs





Organic electronics



Energetic materials

Research in our group

Expertiese

- Molecular modeling
- Organic synthesis
- Organometallic synthesis
- Homogeneous catalysis
- Physical methods

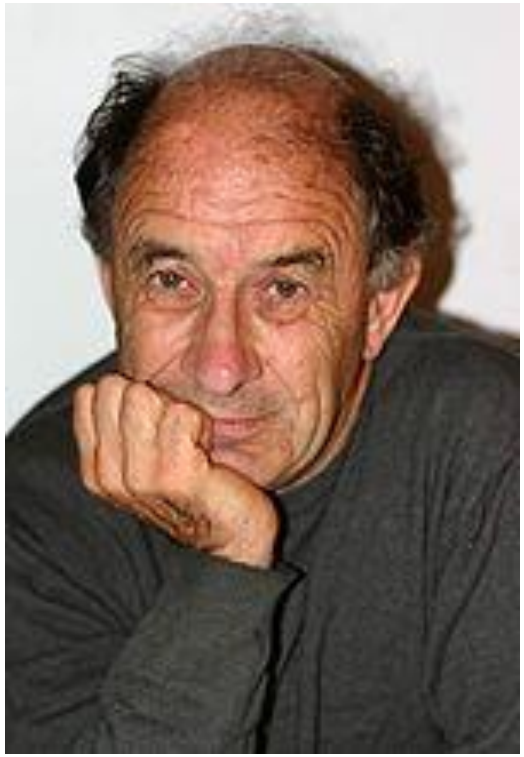
Interdisciplinary approach to solve problems

From science to industry

Academic collaborations

Contract research ~ 80 % funding of our group

Vladimir Arnold



Vladimir Igorevich Arnold

1937 – 2010

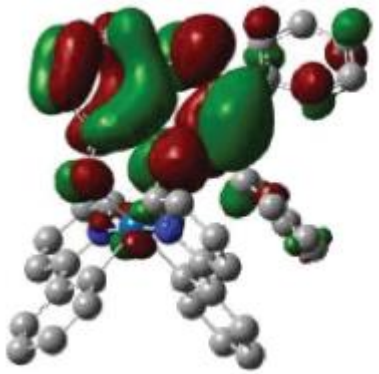
There is no “fundamental or applied” science. There is science and its applications.

Science gives us a key for understanding of the nature and instruments to solve vital problems.

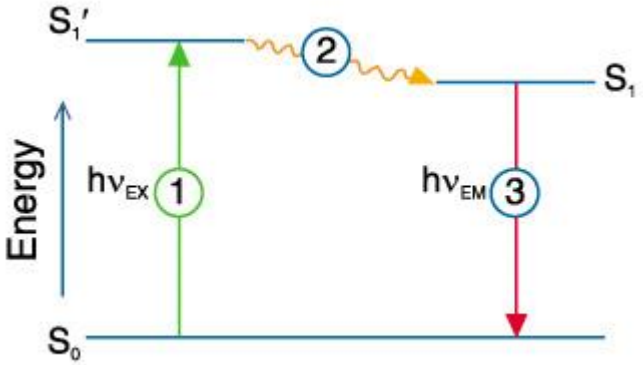
Molecular modeling

State of the art QM techniques enable studies of complex structures with high precision

Electronic structure



Spectral properties



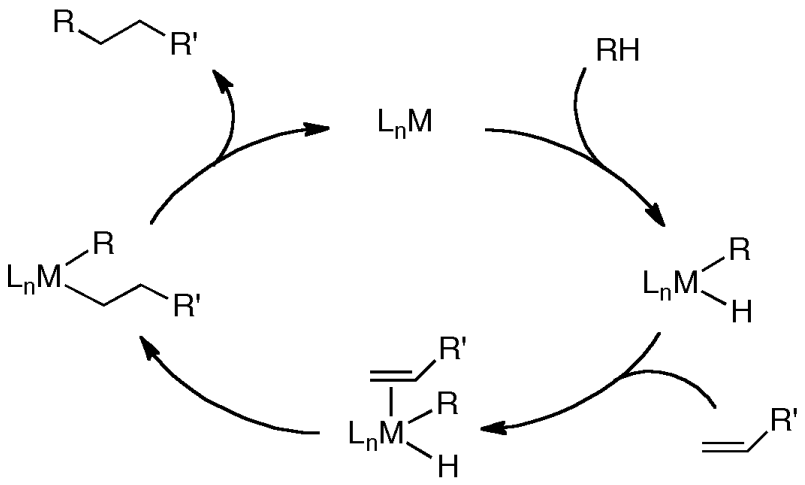
Molecular modeling

Thermochemistry

Reaction energetics
Stability of structures

Catalysis

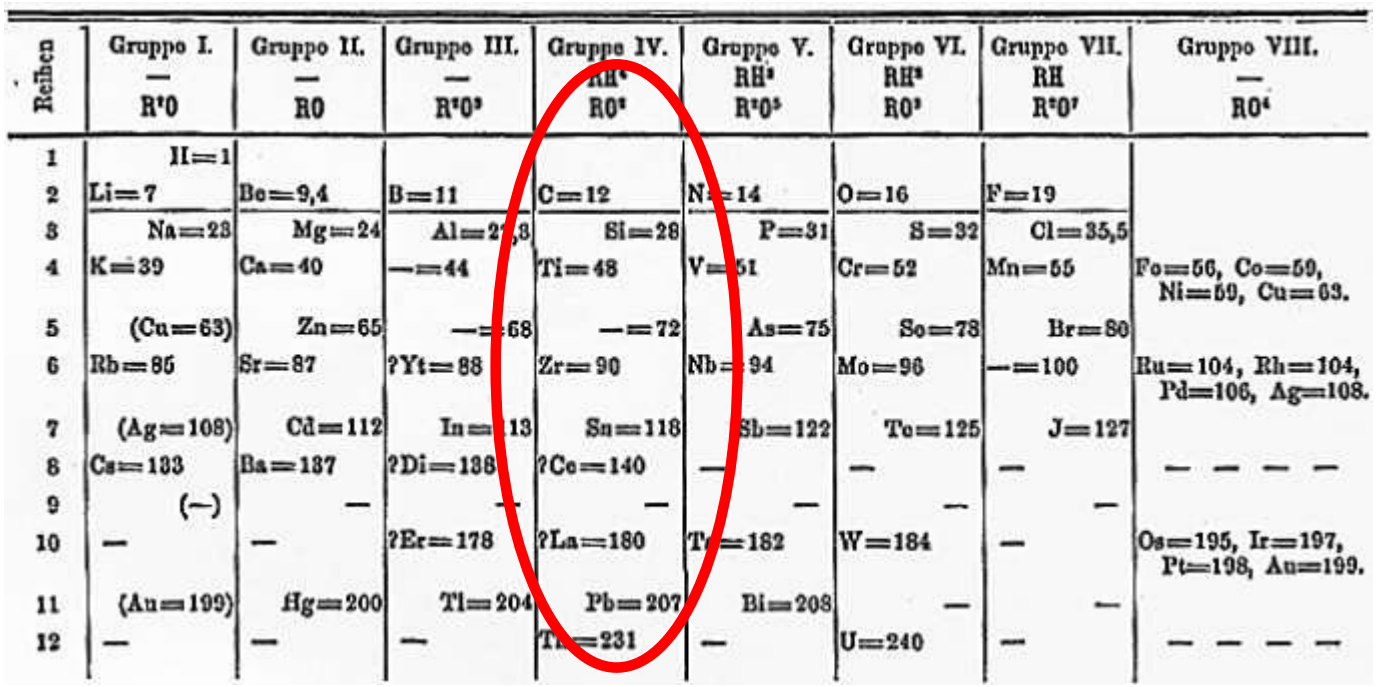
Reaction mechanism
Inverse problem



Carbon group elements chemistry

C Si Ge Sn Pb

Dmitry Ivanovich Mendeleev (1871):



Reihen	Gruppo I. — R^1O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppo IV. RH^4 RO^2	Gruppo V. RH^3 R^2O^5	Gruppo VI. RH^2 RO^3	Gruppo VII. RH R^2O^7	Gruppo VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Prediction of Germanium

Was known:	$Si(C_2H_5)_4$	-	$Sn(C_2H_5)_4$
Predicted:	Eka-$Si(C_2H_5)_4$	d = 0.96 g/ml	T_b = 160°C
C. Winkler (1887):	$Ge(C_2H_5)_4$	d = 0.99 g/ml	T_b = 163.5°C

Periodicity

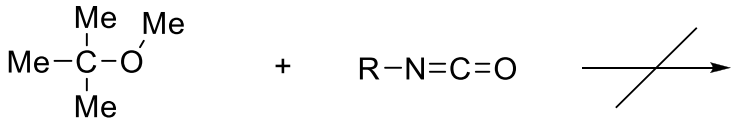
Increase in atomic number

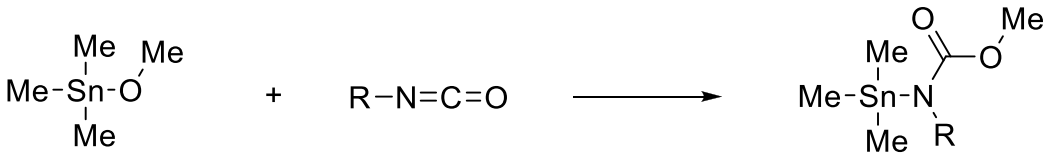
Increase in atom volume, bond length

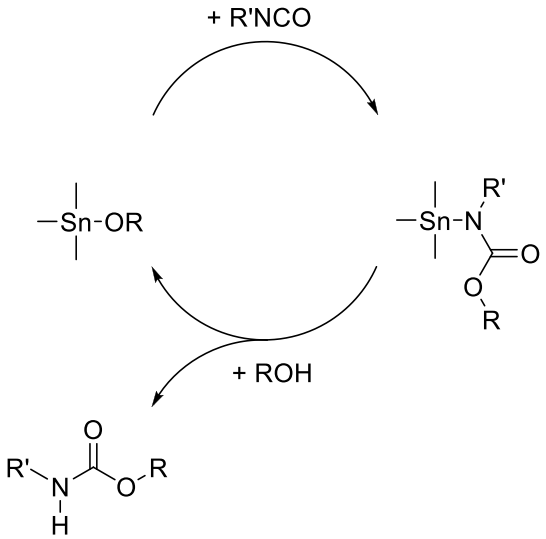
Decrease in bond energy E-E, E-C

Increase in polarizability

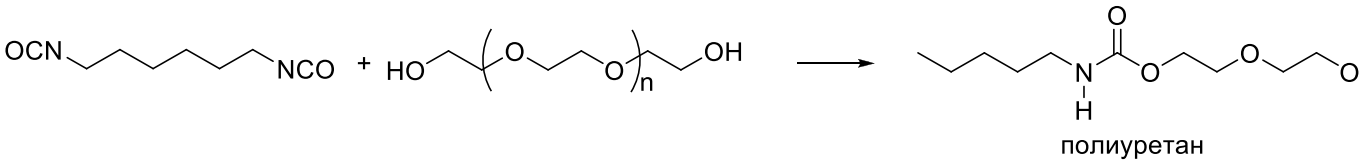
Chemical properties

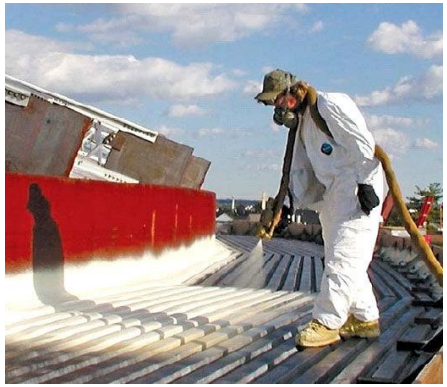


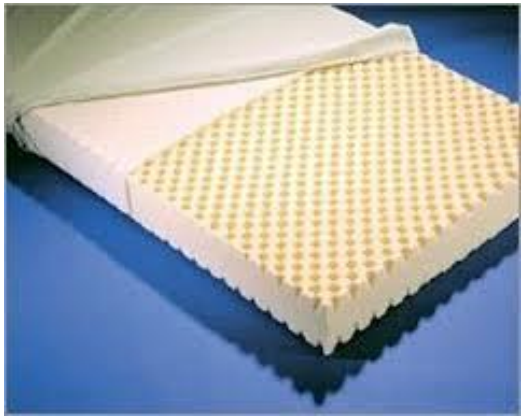




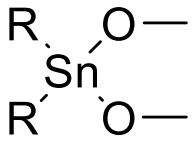
Polyurethanes



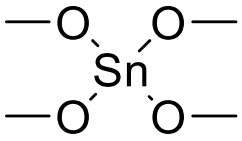




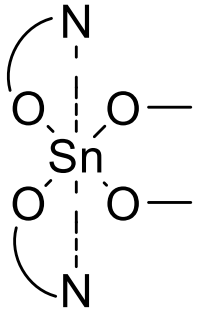
Non-toxic catalysts, design



High activity, toxic

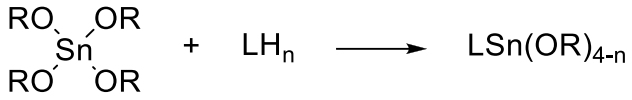


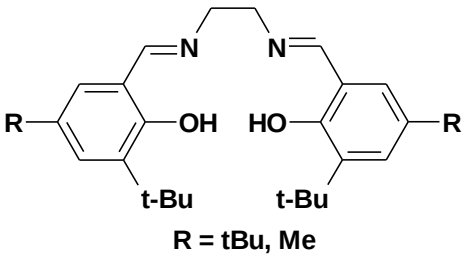
No Sn-C bond - no toxicity
Active
Low stability

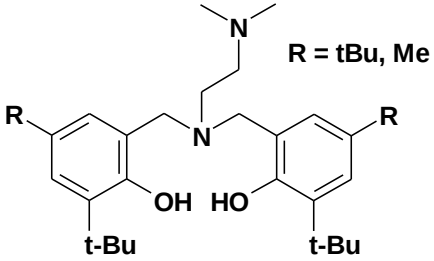


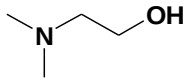
Not toxic
Stable

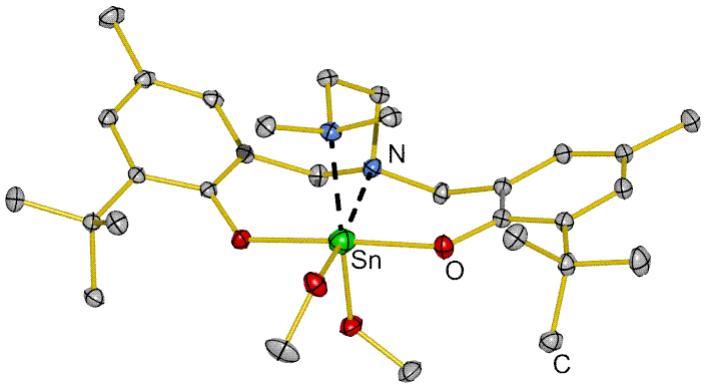
Non-toxic catalysts, synthesis

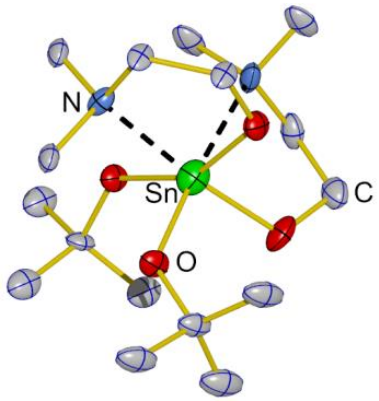




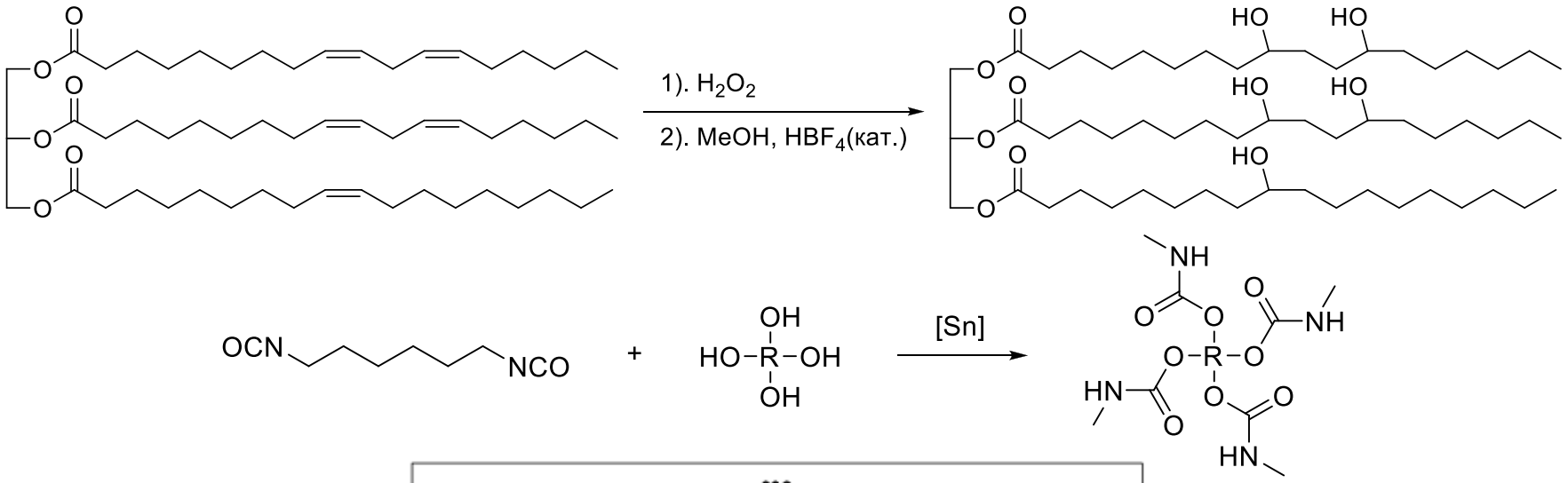


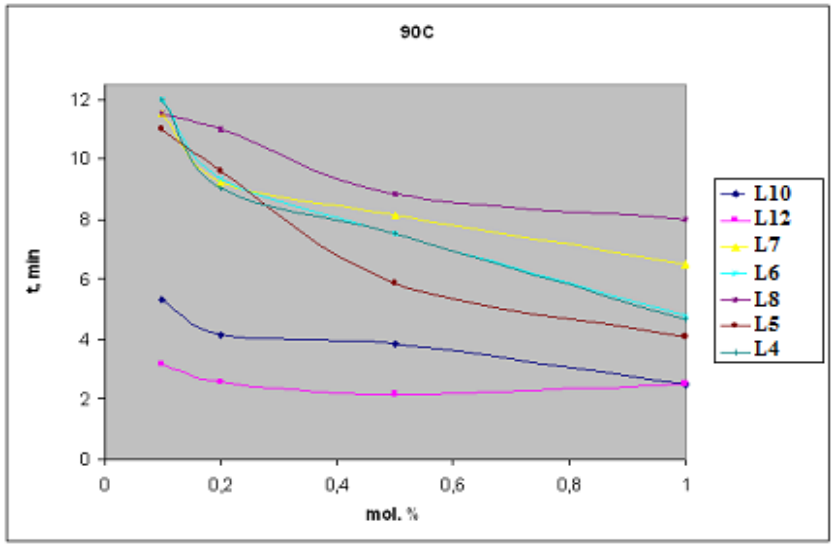






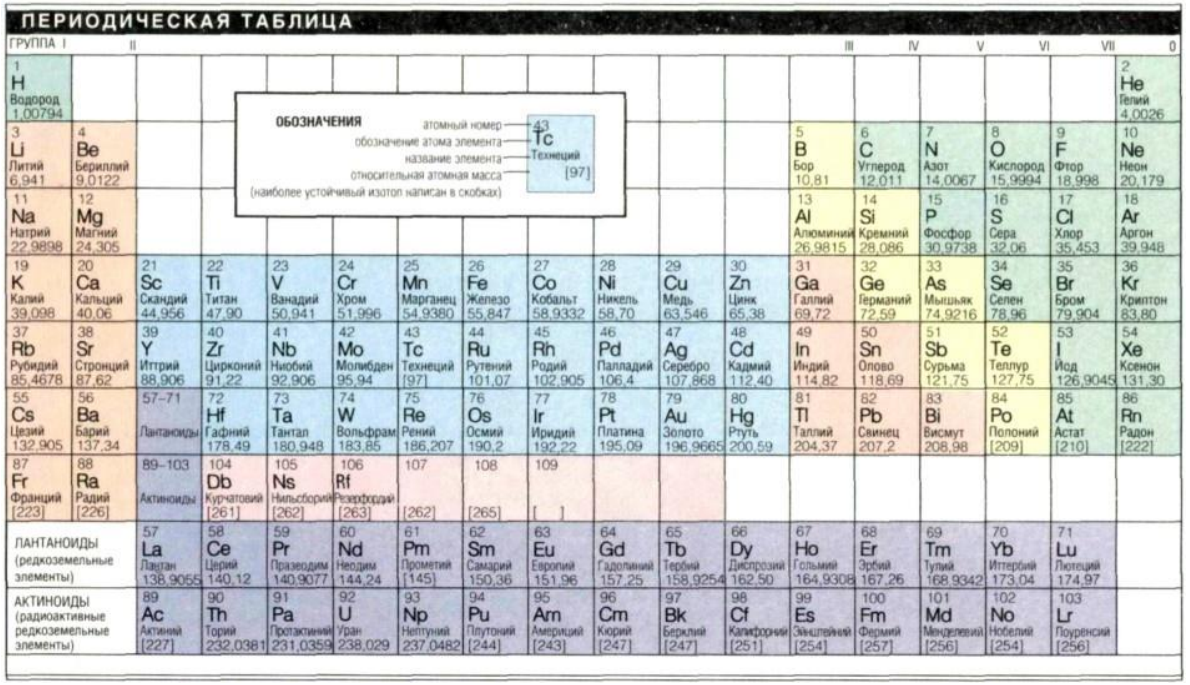
Non-toxic catalysts, application





Organometallic chemistry – chemistry of ligands

Not too much available metals!



ПЕРИОДИЧЕСКАЯ ТАБЛИЦА

ГРУППА I II III IV V VI VII 0

1 H Водород 1,00794																2 He Гелий 4,0026
3 Li Литий 6,941	4 Be Бериллий 9,0122											5 B Бор 10,81	6 C Углерод 12,011	7 N Азот 14,0067	8 O Кислород 15,9994	9 F Фтор 18,998	10 Ne Неон 20,179
11 Na Натрий 22,9898	12 Mg Магний 24,305											13 Al Алюминий 26,9815	14 Si Кремний 28,086	15 P Фосфор 30,9738	16 S Сера 32,06	17 Cl Хлор 35,453	18 Ar Аргон 39,948
19 K Калий 39,098	20 Ca Кальций 40,06	21 Sc Скандий 44,956	22 Ti Титан 47,90	23 V Ванадий 50,941	24 Cr Хром 51,996	25 Mn Марганец 54,9380	26 Fe Железо 55,847	27 Co Кобальт 58,9332	28 Ni Никель 58,70	29 Cu Медь 63,546	30 Zn Цинк 65,38	31 Ga Галлий 69,72	32 Ge Германий 72,59	33 As Мышьяк 74,9216	34 Se Селен 78,96	35 Br Бром 79,904	36 Kr Криптон 83,80
37 Rb Рубидий 85,4678	38 Sr Стронций 87,62	39 Y Иттрий 88,906	40 Zr Цирконий 91,22	41 Nb Ниобий 92,906	42 Mo Молибден 95,94	43 Tc Технеций [97]	44 Ru Рутений 101,07	45 Rh Родий 102,905	46 Pd Палладий 106,4	47 Ag Серебро 107,868	48 Cd Кадмий 112,40	49 In Индий 114,82	50 Sn Олово 118,69	51 Sb Сурьма 121,75	52 Te Теллур 127,75	53 I Йод 126,9045	54 Xe Ксенон 131,30
55 Cs Цезий 132,905	56 Ba Барий 137,34	57–71 Лантаноиды	72 Hf Гафний 178,49	73 Ta Тантал 180,948	74 W Вольфрам 183,85	75 Re Рений 186,207	76 Os Осмий 190,2	77 Ir Иридий 192,22	78 Pt Платина 195,09	79 Au Золото 196,9665	80 Hg Ртуть 200,59	81 Tl Таллий 204,37	82 Pb Свинец 207,2	83 Bi Висмут 208,98	84 Po Полоний [209]	85 At Астат [210]	86 Rn Радон [222]
87 Fr Франций [223]	88 Ra Радий [226]	89–103 Актиноиды	104 Db Курчатовий [261]	105 Ns Нильсборий [262]	106 Rf Резерфордий [263]	107 [262]	108 [265]	109 [ ]									
ЛАНТАНОИДЫ (редкоземельные элементы)		57 La Лантан 138,9055	58 Ce Церий 140,12	59 Pr Празеодим 140,9077	60 Nd Неодим 144,24	61 Pm Прометий [145]	62 Sm Самарий 150,36	63 Eu Европий 151,96	64 Gd Гадолиний 157,25	65 Tb Тербий 158,9254	66 Dy Диспрозий 162,50	67 Ho Гольмий 164,9303	68 Er Эрбий 167,26	69 Tm Тулий 168,9342	70 Yb Иттербий 173,04	71 Lu Лютеций 174,97	
АКТИНОИДЫ (радиоактивные редкоземельные элементы)		89 Ac Актиний [227]	90 Th Торий 232,0381	91 Pa Протактиний 231,0359	92 U Уран 238,029	93 Np Нептуний 237,0482	94 Pu Плутоний [244]	95 Am Америций [243]	96 Cm Кюрий [247]	97 Bk Берклий [247]	98 Cf Калифорний [251]	99 Es Эйнштейний [254]	100 Fm Фермий [257]	101 Md Менделевий [256]	102 No Нобелий [254]	103 Lr Лоуренсий [256]	

ОБОЗНАЧЕНИЯ
атомный номер — 43
обозначение атома элемента — Tc
название элемента — Технеций
относительная атомная масса — [97]
(наиболее устойчивый изотоп написан в скобках)

Ti, V, Cr, Fe, Co, Ni, Cu, Ln Pd, Pt, Au Rh, Ir

Divalent compounds

C

Si

Ge

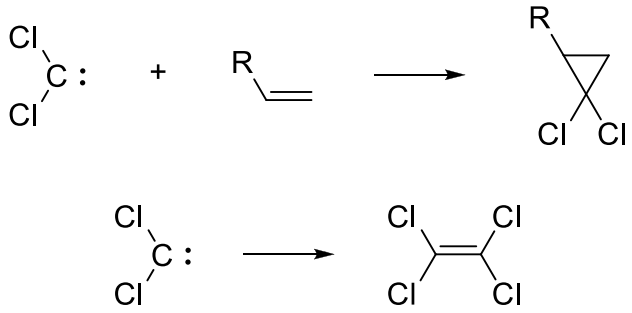
Sn

Pb

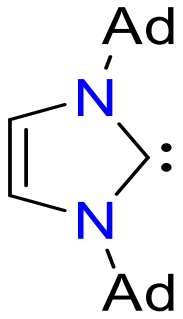
Increase in stability of divalent derivatives

$SnCl_2$, $PbCl_2$ – stable

CCl_2 – highly reactive

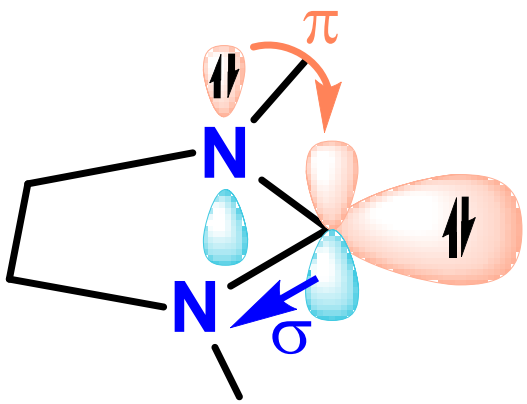


Stable carbenes

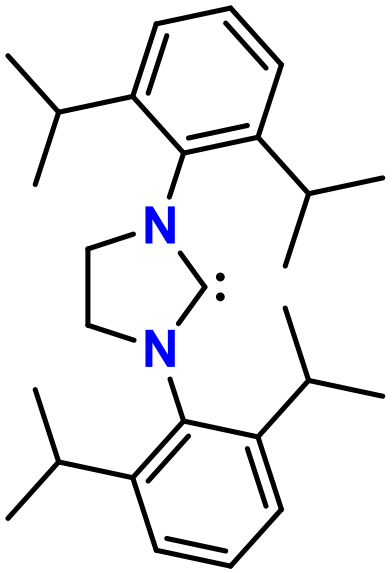


T. Arduengo III Jr., 1991

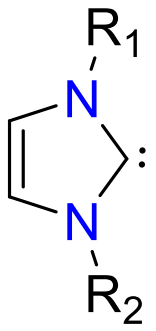
Electronic

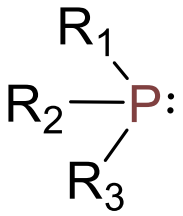


Steric



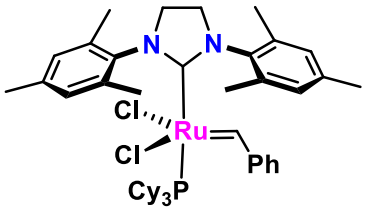
Properties of stable carbenes





- Stronger donors
- More stable complexes
- Synthetic accessibility
- Easily functionalized
- Lower toxicity

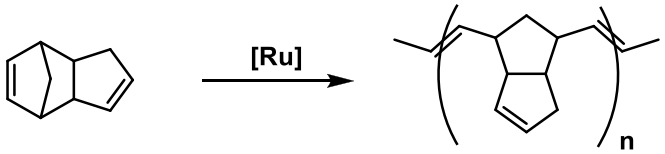
Applications of stable carbenes



Grubbs II

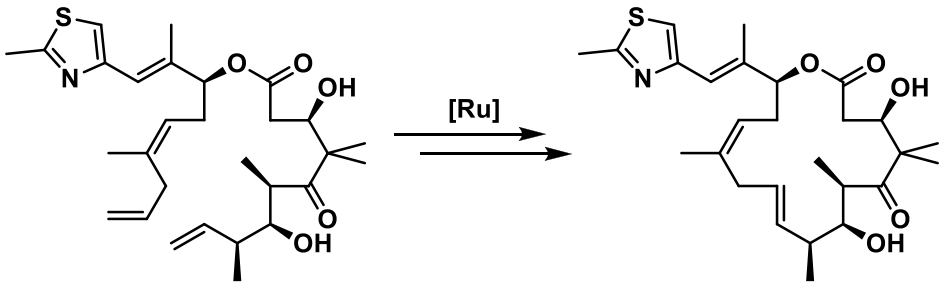
Polymerizations

car palstics

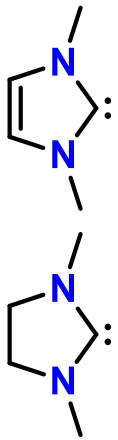


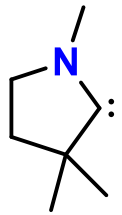
Synthesis of new drugs

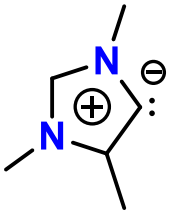
Hoffman-La Roche, C_{16} cycle

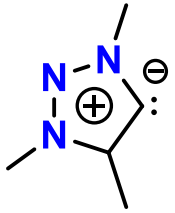


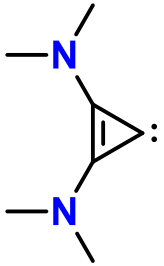
New types of stable carbenes

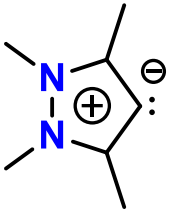


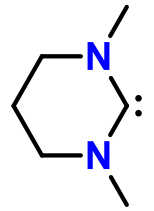


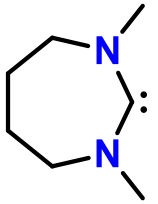




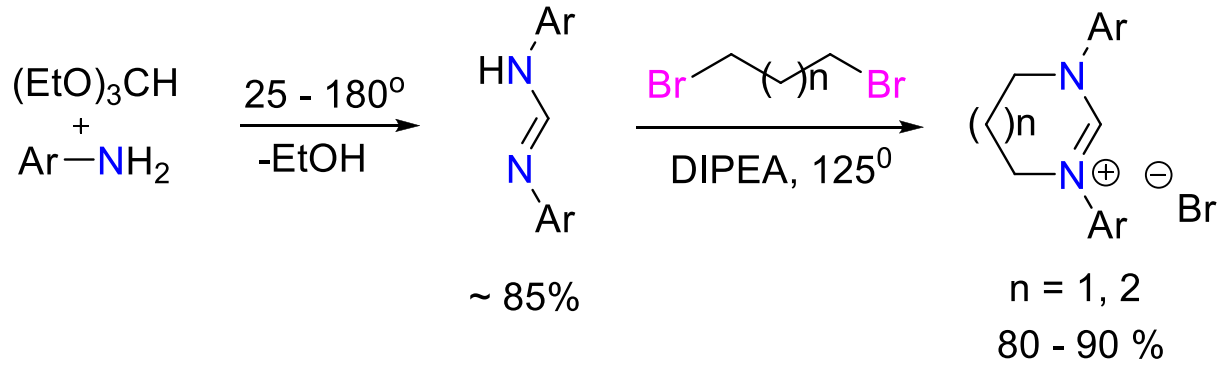


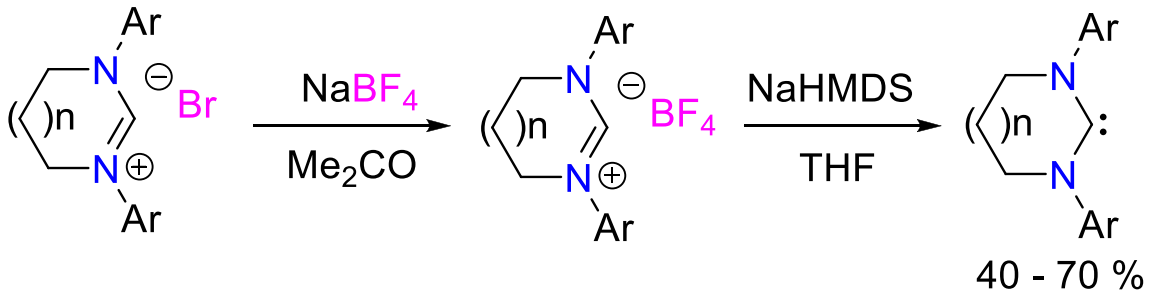




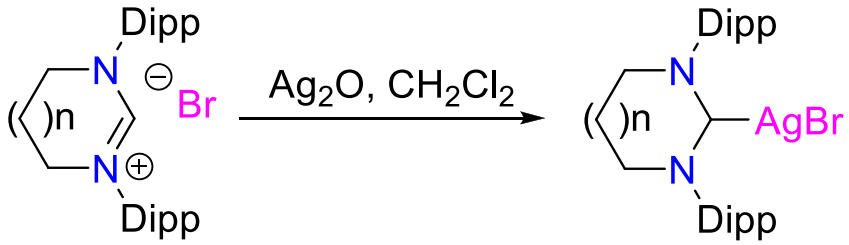


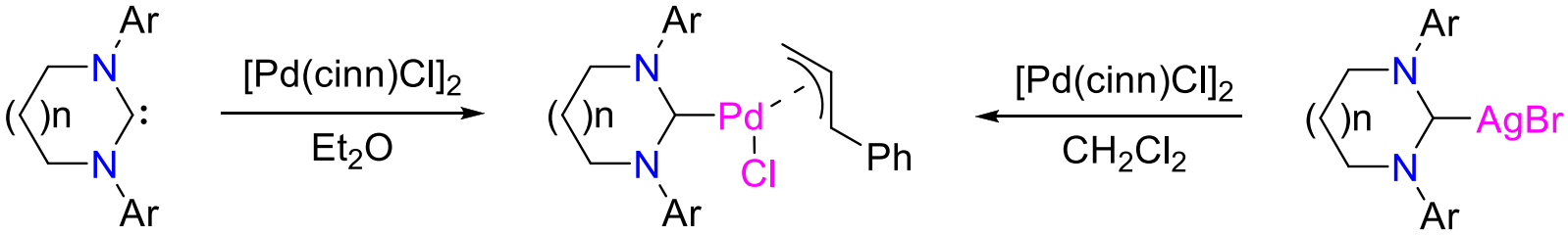
Synthesis of carbenes





Carbene complexes

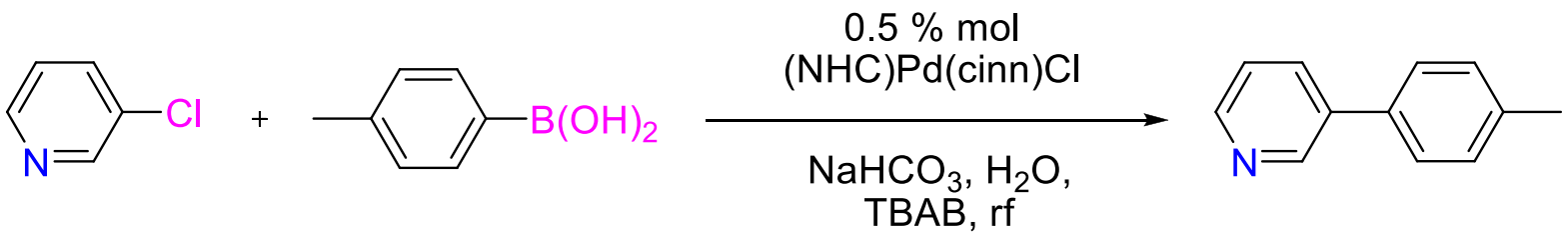




n = 0, 1, 2; Ar = Mes, Dipp

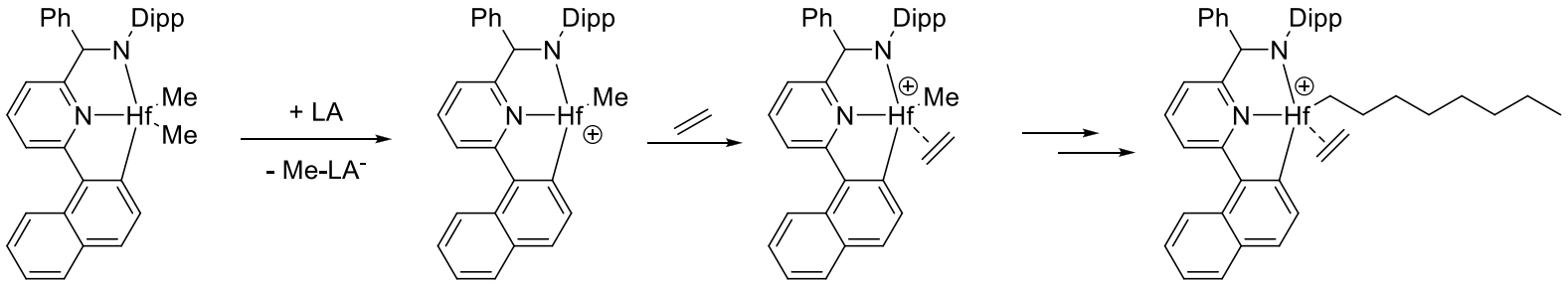
35 - 95 %

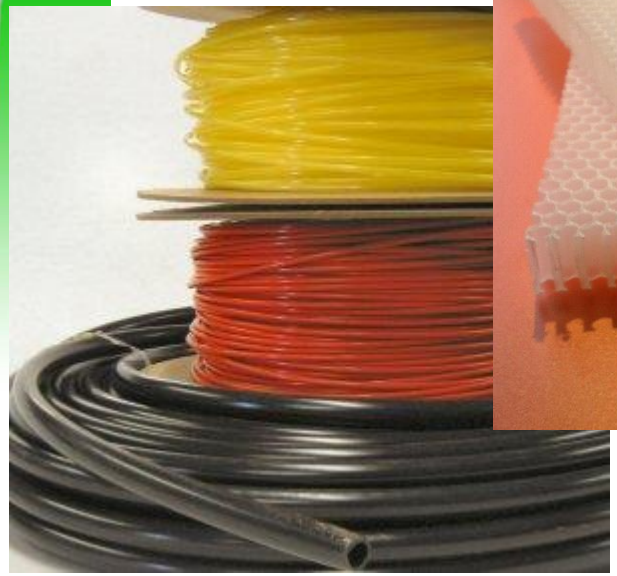
Suzuki-Miyaura reaction

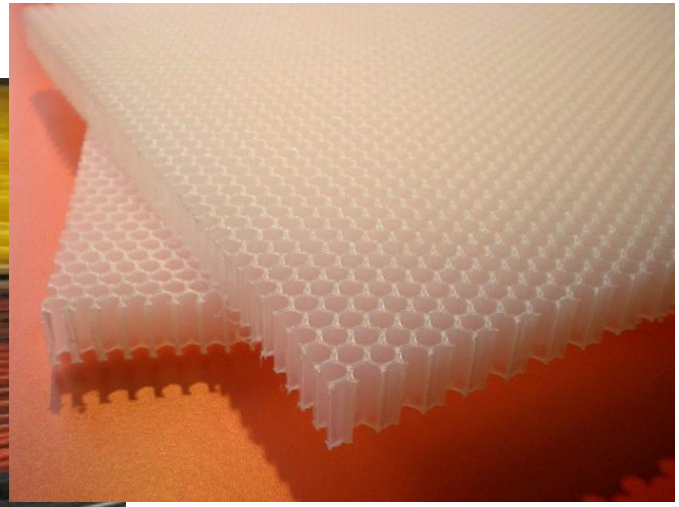


- Pure water, no organic solvents
- In air, no oxidation of ligands
- Low loading of metal (0.5 mol%)
- High reaction rate (30 – 60 min)
- No side products

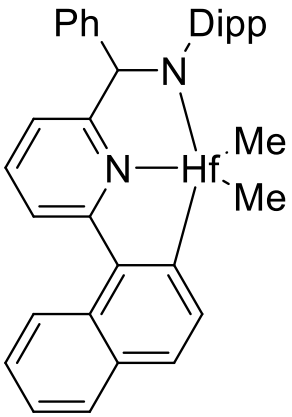
Polyolefines

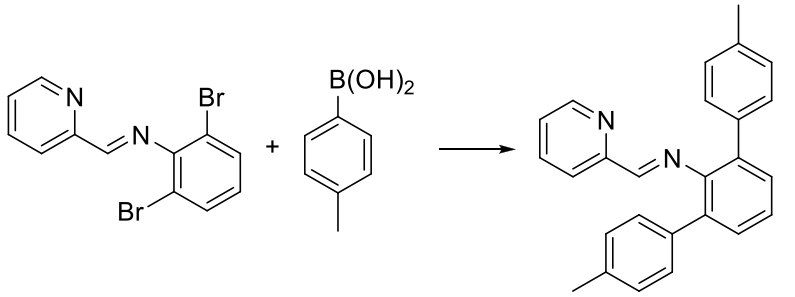


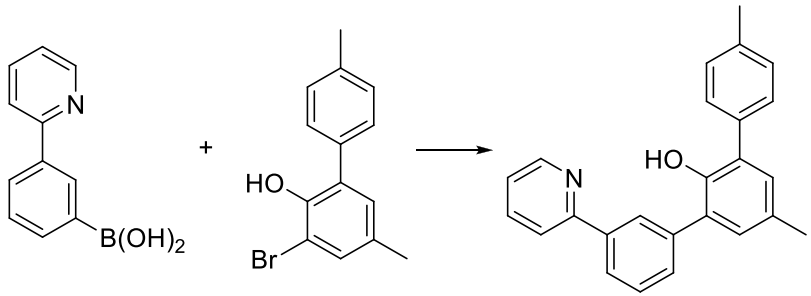




New catalysts







Applied research

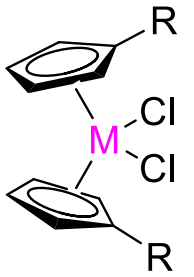
- Catalysts for PO synthesis
- Catalysts for rubber synthesis
- Biodegradable polymers
- Organic electronics materials

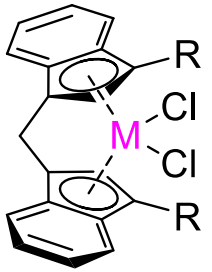
Catalysts for PO synthesis

10+ years experience in PE/PP catalysts

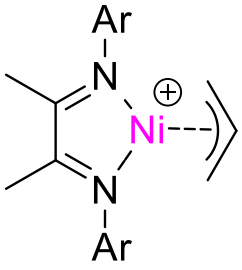
New generations of catalysts

Metallocenes

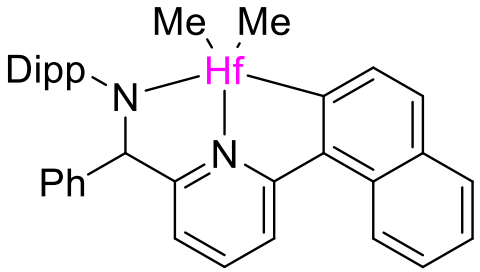




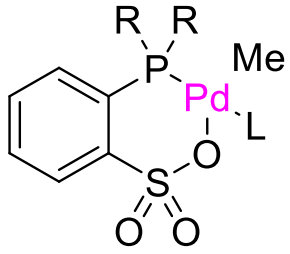
Post-metallocenes



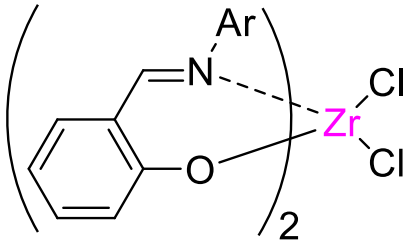
Brookhart



Dow



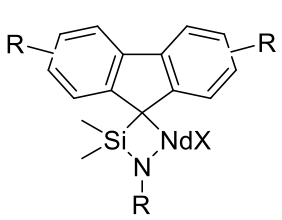
Drent

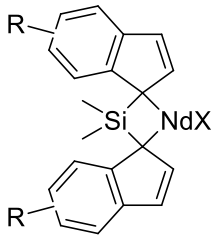


Fujita

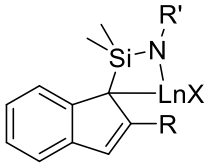
Catalysts for rubber synthesis

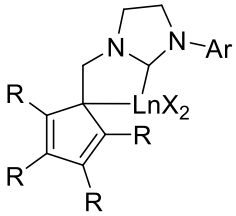
Ethylene-butadiene rubber (EBR)

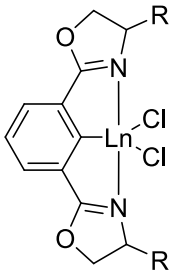




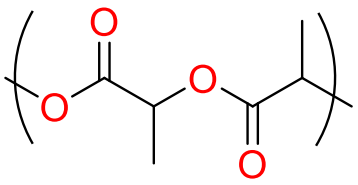
High-cis PB and PI rubber







Biodegradable polymers



polylactide

New types of catalysts: Sn, Al

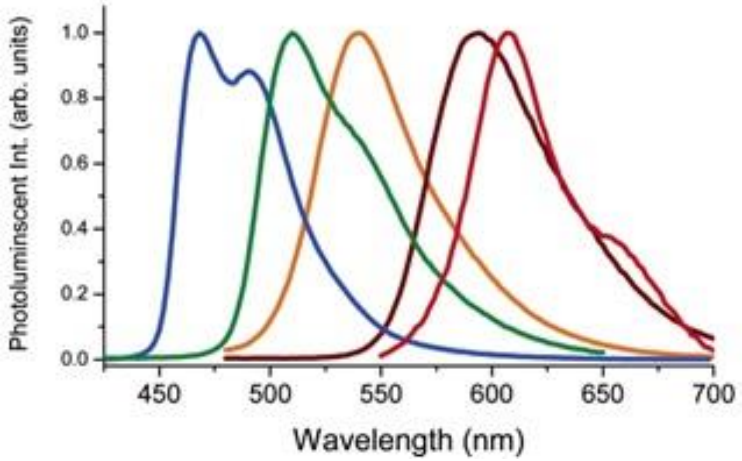
Highly active and selective: Ti, Zr, Hf-postmetallocenes

Organic electronics materials

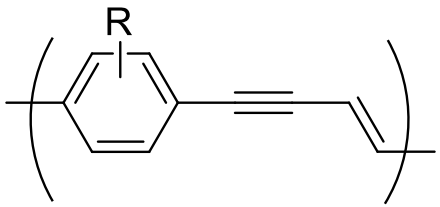
New Ir OLED emitters

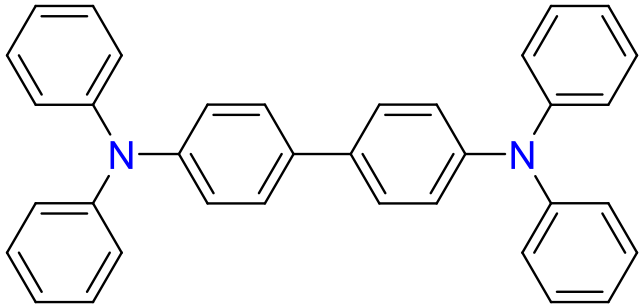
NHC-Ir cyclometallated complexes

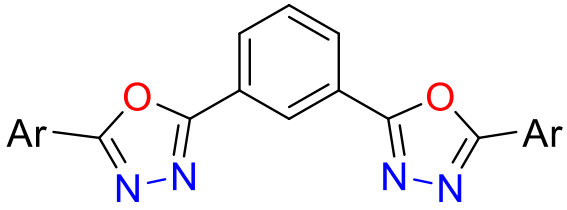
as promissing OLED emitters



New conducting polymers & semiconductors



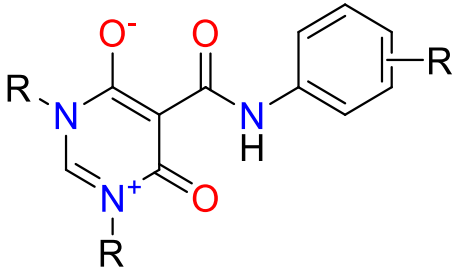




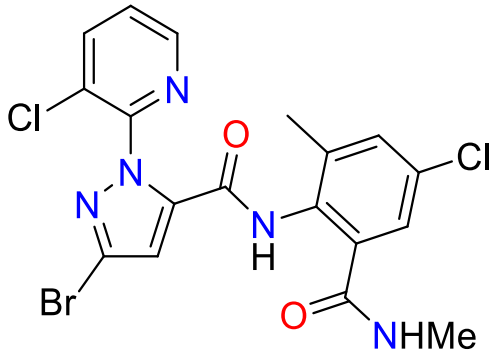
Agrochemistry

- Green chemical technologies
- Optimization and scale-up

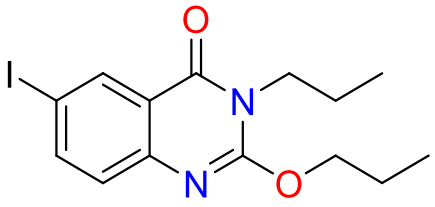
Pesticides



Insecticides



Fungicides



Concluding remarks

- Organics are all around
- There is no need for molecules, but there is a need in molecular properties
- Property – Structure – Synthesis – Application
- Organometallic chemistry in a chemistry of ligands
- There is no “fundamental or applied” science! There is science and its applications.

Contacts

Mikhail S. Nechaev, Ph. D., D. Sc.

Department of Chemistry, MSU

mob.: +7 (903) 250 60 80
e-mail: m.s.nechaev@org.chem.msu.ru