TRANSITION METAL CATALYSTS FOR OLEFIN POLYMERIZATIONS : NOVEL POLYMER STRUCTURES AND FUNCTIONAL POLYOLEFINS

IV th Russian Indian Symposium Catalysis and Environmental Engineering
St. Petersburg
September 15-16, 2013

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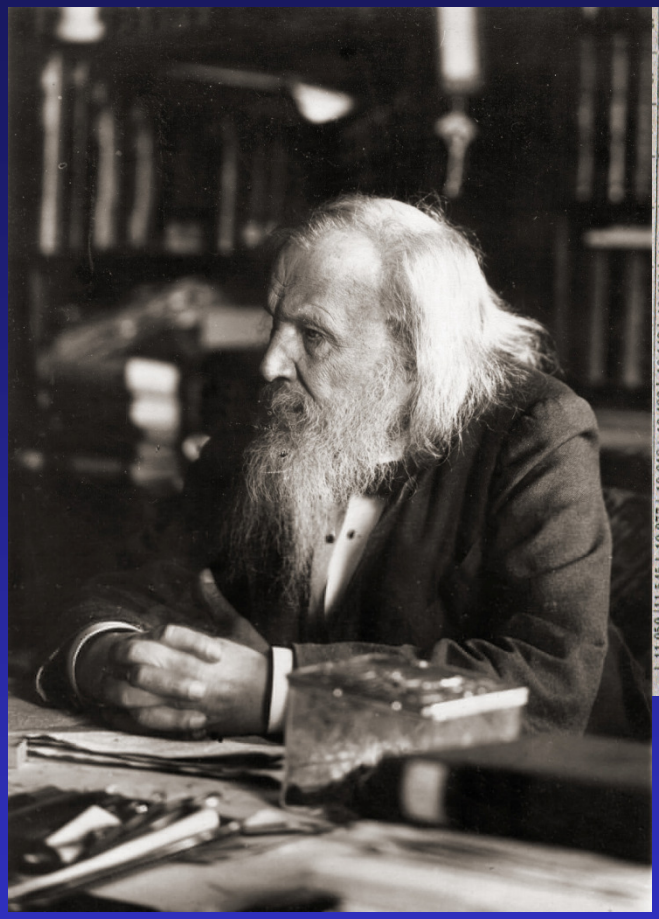
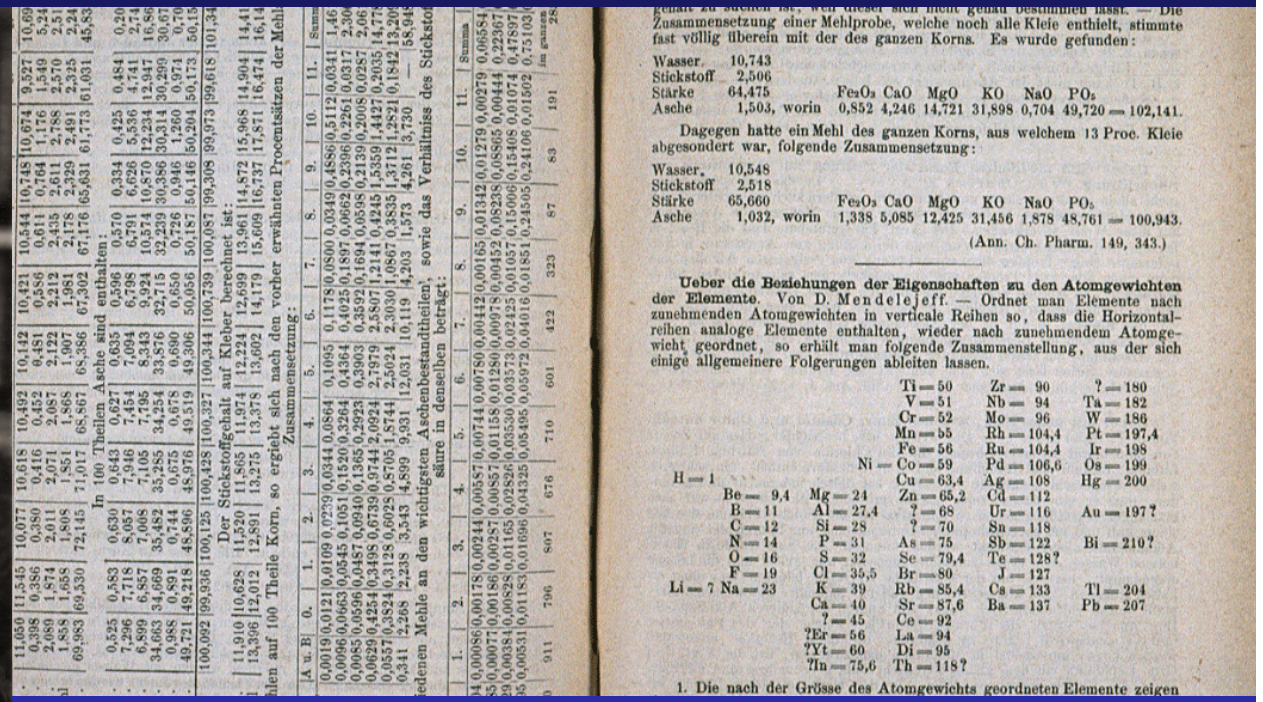




Zusammensetzung einer Mehlprobe, welche noch alle Kleie enthielt, stimmte fast völlig überein mit der des ganzen Korns. Es wurde gefunden:

Wasser	10,743							
Stickstoff	2,506							
Stärke	64,475							
Asche	1,503, worin	Fe_2O_3	CaO	MgO	KO	NaO	PO_5	
		0,852	4,246	14,721	31,898	0,704	49,720	= 102,141.

Dagegen hatte ein Mehl des ganzen Korns, aus welchem 13 Proc. Kleie abgesondert war, folgende Zusammensetzung:

Wasser	10,548							
Stickstoff	2,518							
Stärke	65,660							
Asche	1,032, worin	Fe_2O_3	CaO	MgO	KO	NaO	PO_5	
		1,338	5,085	12,425	31,456	1,878	48,761	= 100,943.

(Ann. Ch. Pharm. 149, 343.)

Ueber die Beziehungen der Eigenschaften zu den Atomgewichten der Elemente. Von D. Mendelejeff. — Ordnet man Elemente nach zunehmenden Atomgewichten in verticale Reihen so, dass die Horizontalreihen analoge Elemente enthalten, wieder nach zunehmendem Atomgewicht geordnet, so erhält man folgende Zusammenstellung, aus der sich einige allgemeinere Folgerungen ableiten lassen.

				Ti = 50	Zr = 90	? = 180		
				V = 51	Nb = 94	Ta = 182		
				Cr = 52	Mo = 96	W = 186		
				Mn = 55	Rh = 104,4	Pt = 197,4		
				Fe = 56	Ru = 104,4	Ir = 198		
			Ni =	Co = 59	Pd = 106,6	Os = 199		
H = 1				Cu = 63,4	Ag = 108	Hg = 200		
	Be = 9,4	Mg = 24		Zn = 65,2	Cd = 112			
	B = 11	Al = 27,4		? = 68	Ur = 116	Au = 197?		
	C = 12	Si = 28		? = 70	Sn = 118			
	N = 14	P = 31		As = 75	Sb = 122	Bi = 210?		
	O = 16	S = 32		Se = 79,4	Te = 128?			
	F = 19	Cl = 35,5		Br = 80	J = 127			
Li = 7	Na = 23	K = 39		Rb = 85,4	Cs = 133	Tl = 204		
		Ca = 40		Sr = 87,6	Ba = 137	Pb = 207		
		? = 45		Ce = 92				
		?Er = 56		La = 94				
		?Yt = 60		Di = 95				
		?In = 75,6		Th = 118?				

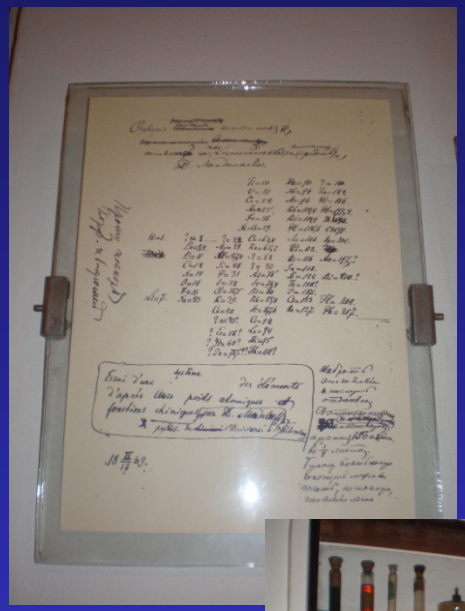
1. Die nach der Grösse des Atomgewichts geordneten Elemente zeigen

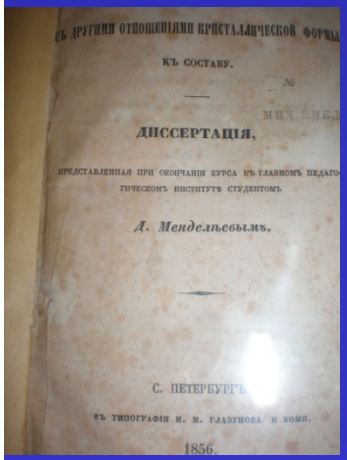
Attempt at a system of elements based on therir atomic weight and chemical affinity in Principles of Chemistry, published in 1870

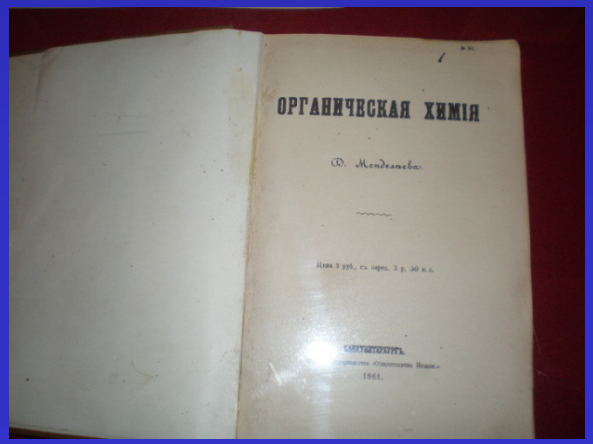
Dimitri MENDELEJEFF
1834-1907

On the Relationships of the Properties to the Atomic Weights of the Elements
D. Mendelejeff,
Zeitschrift für Chemie 12,405-406(1869)

MENDELEEV'S STUDY : ST.PETERSBURG, RUSSIA







Pictures taken on September 16, 2013

THE PERIODIC TABLE

- Immediately after Mendeleev published his Periodic Table, Gallium (1875), Scandium (1879) and Germanium (1886) were discovered in rapid succession, fitting exactly in the Table after Aluminum, Calcium and Silicon. Ramsay's discovery of rare gases (He, Ne, Kr and Xe), however, created a problem for Mendeleev !

- Periodic Table is like a revelation , sprung from the minds of the creator, inherently beautiful !
- It is as if the natural order of the elements was always there, waiting to be discovered
- It is mystical because the Periodic Table does not really exist. It is only a construct of the mind, a sort of mnemonic that helps in easy recall

PERIODIC TABLE OF THE ELEMENTS

SIGMA-ALDRICH Techware™
FROM BENCHTOP TO BOOKSHELF

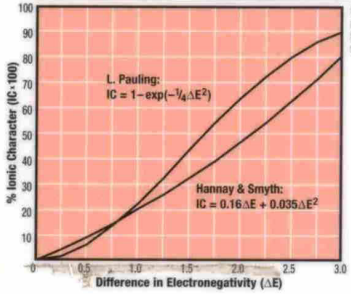
▼ Elementary Subatomic Particles

	Electron	Proton	Neutron	Photon	Neutrino
Symbol	e	P	n	γ	ν
Rest mass (kg)	9.1093897(54) x 10^{-31}	1.6726231(10) x 10^{-27}	1.6749286(10) x 10^{-27}	0	≈ 0
Molar mass (kg/mol)	5.48579903(13) x 10^{-7}	1.007276470(12) x 10^{-3}	1.008664904(14) x 10^{-3}	0	≈ 0
Particle-electron mass ratio	1	1836.152701(37)	1838.683662(40)	0	≈ 0
Particle-proton mass ratio	5.44617013(11) x 10^{-4}	1	1.001378404(9)	0	≈ 0
Particle-neutron mass ratio	5.438673x10^{-4}	0.998624	1	0	≈ 0
Specific charge (C/kg)	−1.75881962(53) x 10^{+11}	9.5788309(29) x 10^{+7}	0	0	0
Radius (m)	< 1 x 10^{-16}	8 x 10^{-16}	8 x 10^{-16}	0	≈ 0
Spin quantum number	1/2	1/2	1/2	1	1/2
Compton wavelength (m)	2.42631058(22) x 10^{-12}	1.32141002(12) x 10^{-15}	1.31959110(12) x 10^{-15}	–	–
Magnetic moment (J/T); μ	928.47701(31) x 10^{-26}	1.41060761(47) x 10^{-26}	0.96623707(40) x 10^{-26}	0	0
in Bohr magnetons; μ/μ_B	1.001159652193(10)	1.521032202(15) x 10^{-3}	1.04187563(25) x 10^{-3}	0	0
in nuclear magnetons; μ/μ_N	1838.282000(37)	2.792847386(63)	1.91304275(45)	0	0

Elementary particles are the fundamental constituents of energy and matter. The positron (e^+) is a positive-energy particle which has the same mass as an ordinary electron. The antineutrino ($\bar{\nu}$) has similar properties as that of a neutrino (ν) except its spin is directed along its direction of motion, whereas the neutrino's spin is always opposite to the direction of motion. Negative beta decay is the transformation of a neutron into a proton, a beta particle (negative electron) and a antineutrino ($n \rightarrow p + e^- + \bar{\nu}$). Positive beta decay involves the transformation of a proton into a neutron, a positron and a neutrino ($p \rightarrow n + \beta^+ + \nu$). The magnetic moment ($\mu$) of a particle can also be expressed as a dimensionless quantity by dividing it with either the Bohr magneton (μ_B = 9.2740154(31) x 10^{-24} J/T) or the nuclear magneton (μ_N = 5.0507866(17) x 10^{-27} J/T).

▼ % Ionic Character of a Single Chemical Bond

Difference in Electronegativity	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2
% IC (by L. Pauling)	0.2	1.0	2.2	3.9	6.1	8.6	12	15	18	22	26	30	34	39	43	47	51	56	59	63	67	70	73	76	79	82	84	86	88	89	91	92
% IC (by Hannay & Smyth)	1.6	3.3	5.1	7.0	8.9	11	13	15	17	20	22	24	27	29	32	35	37	40	43	46	49	52	55	59	62	65	69	72	76	80	83	87



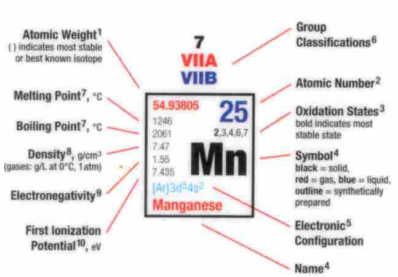
Percent ionic character describes the nature of a bond. Bonds possessing 50% or greater ionic character are commonly termed ionic; bonds with less than 50% ionic character are termed covalent. Pauling's equation was modified by Hannay & Smyth in order to achieve better agreement between experimental and calculated values. Transition from ionic to covalent binding is usually accompanied by a reduction in electrical conductance, melting point and boiling point.

1 IA IA	2 IIA IIA	3 IIIA IIIB	4 IVA IVB	5 VA VB	6 VIA VIB	7 VIIA VIIB	8 VIIIA VIII	9 VIIIA VIII	10 VIIIA VIII	11 IB IB	12 IIB IIB	13 IIIB IIIA	14 IVB IVA	15 VB VA	16 VIB VIA	17 VIIB VIIA	18 VIII 0
1.00794 1 H Hydrogen																	4.002602 2 He Helium
6.941 3 Li Lithium	9.012182 4 Be Beryllium											10.811 5 B Boron	12.011 6 C Carbon	14.00674 7 N Nitrogen	15.9994 8 O Oxygen	18.9984032 9 F Fluorine	20.1797 10 Ne Neon
22.989768 11 Na Sodium	24.3050 12 Mg Magnesium											26.981539 13 Al Aluminum	28.0855 14 Si Silicon	30.973762 15 P Phosphorus	32.066 16 S Sulfur	35.4527 17 Cl Chlorine	39.948 18 Ar Argon
39.0983 19 K Potassium	40.078 20 Ca Calcium	44.955910 21 Sc Scandium	47.88 22 Ti Titanium	50.9415 23 V Vanadium	51.9961 24 Cr Chromium	54.93805 25 Mn Manganese	55.847 26 Fe Iron	58.93320 27 Co Cobalt	58.6934 28 Ni Nickel	63.546 29 Cu Copper	65.39 30 Zn Zinc	69.723 31 Ga Gallium	72.61 32 Ge Germanium	74.92159 33 As Arsenic	78.96 34 Se Selenium	79.904 35 Br Bromine	83.80 36 Kr Krypton
85.4678 37 Rb Rubidium	87.62 38 Sr Strontium	88.90585 39 Y Yttrium	91.224 40 Zr Zirconium	92.90638 41 Nb Niobium	95.94 42 Mo Molybdenum	(97.9072) 43 Tc Technetium	101.07 44 Ru Ruthenium	102.90550 45 Rh Rhodium	106.42 46 Pd Palladium	107.8682 47 Ag Silver	112.411 48 Cd Cadmium	114.818 49 In Indium	118.710 50 Sn Tin	121.757 51 Sb Antimony	127.60 52 Te Tellurium	126.90447 53 I Iodine	131.29 54 Xe Xenon
132.90543 55 Cs Cesium	137.327 56 Ba Barium	138.9055 57 La Lanthanum	178.49 72 Hf Hafnium	180.9479 73 Ta Tantalum	183.84 74 W Tungsten	186.207 75 Re Rhenium	190.23 76 Os Osmium	192.22 77 Ir Iridium	195.08 78 Pt Platinum	196.96654 79 Au Gold	200.59 80 Hg Mercury	204.3833 81 Tl Thallium	207.2 82 Pb Lead	208.98037 83 Bi Bismuth	(208.9824) 84 Po Polonium	(209.9871) 85 At Astatine	(222.0176) 86 Rn Radon
(223.0197) 87 Fr Francium	(226.0254) 88 Ra Radium	(227.0278) 89 Ac Actinium	(261.11) 104 Unq Unnilquadium	(262.114) 105 Unp Unnilpentium	(263.118) 106 Unh Unnilhexium	(262.12) 107 Uns Unnilseptium	(265) 108 Uno Unniloctium	(266) 109 Une Unnilennium	(272) 110 Uun Ununnium								

**	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
	140.115	140.90765	144.24	(144.9127)	150.36	151.965	157.25	158.92534	162.50	164.93032	167.26	168.93421	173.04	174.967
	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
	[Xe]$4f^1 5d^1 6s^2$	[Xe]$4f^3 6s^2$	[Xe]$4f^4 6s^2$	[Xe]$4f^5 6s^2$	[Xe]$4f^6 6s^2$	[Xe]$4f^7 6s^2$	[Xe]$4f^7 5d^1 6s^2$	[Xe]$4f^9 6s^2$	[Xe]$4f^{10} 6s^2$	[Xe]$4f^{11} 6s^2$	[Xe]$4f^{12} 6s^2$	[Xe]$4f^{13} 6s^2$	[Xe]$4f^{14} 6s^2$	[Xe]$4f^{14} 5d^1 6s^2$

**	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium
	232.0381	231.03588	238.0289	(237.0482)	(244.0642)	(243.0614)	(247.0703)	(247.0703)	(251.0796)	(252.083)	(257.0951)	(258.10)	(259.1009)	(262.11)
	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lawrencium
	[Rn]$6d^2 7s^2$	[Rn]$5f^2 6d^1 7s^2$	[Rn]$5f^3 6d^1 7s^2$	[Rn]$5f^4 6d^1 7s^2$	[Rn]$5f^6 7s^2$	[Rn]$5f^7 7s^2$	[Rn]$5f^7 6d^1 7s^2$	[Rn]$5f^9 7s^2$	[Rn]$5f^{10} 7s^2$	[Rn]$5f^{11} 7s^2$	[Rn]$5f^{12} 7s^2$	[Rn]$5f^{13} 7s^2$	[Rn]$5f^{14} 7s^2$	[Rn]$5f^{14} 6d^1 7s^2$

*Indicates approximate values and/or inconsistent literature data.



The data for this reference guide were obtained from the latest scientific and government sources (IUPAC, CODATA, National Bureau of Standards, etc.). Estimated values and/or inconsistent data are marked with an asterisk (*).

1. Ratio of the average mass per atom of the element to 1/12 of the mass of an atom of ^{12}C. Round brackets indicate atomic weight of the most stable or best known isotope. **2.** Number of protons in the nucleus of each atom of an element. **3.** Number of charges an atom would have in a molecule (or an ionic compound) if electrons were transferred completely. **4.** Names and symbols of elements 104-110 are those recommended by the International Union of Pure and Applied Chemistry (IUPAC)—alternative names have been proposed by other groups. **5.** Distribution of electrons among the various atomic orbitals. **6.** Two older group classifications systems still in use today rely on an A/B coding scheme to categorize periodic properties. Because of the potential for confusion between these two systems (i.e., VIIA in one scheme is equal to VIIB in the other), IUPAC recommends the use of an unambiguous 1-18 group classification system. **7.** Melting point: temperature at which solid and liquid phases coexist in equilibrium. Boiling point: temperature at which the vapor pressure of a liquid is equal to the external atmospheric pressure. Unless otherwise stated values are at 1 atm; SP = sublimation point at 1 atm; TP = triple point. **8.** Mass of the substance divided by its volume (g/cm³ at 20°C; for gases: g/L at 0°C, 1 atm). **9.** Relative measure of the attraction of an atom in a chemical bond for the shared electrons. **10.** Minimum energy to remove an electron from an isolated atom in its ground state (1eV = 96.487 kJ/mol).

Contributors: T. K. Varga, M.A.Sc., C. Bello, M.A.Sc.

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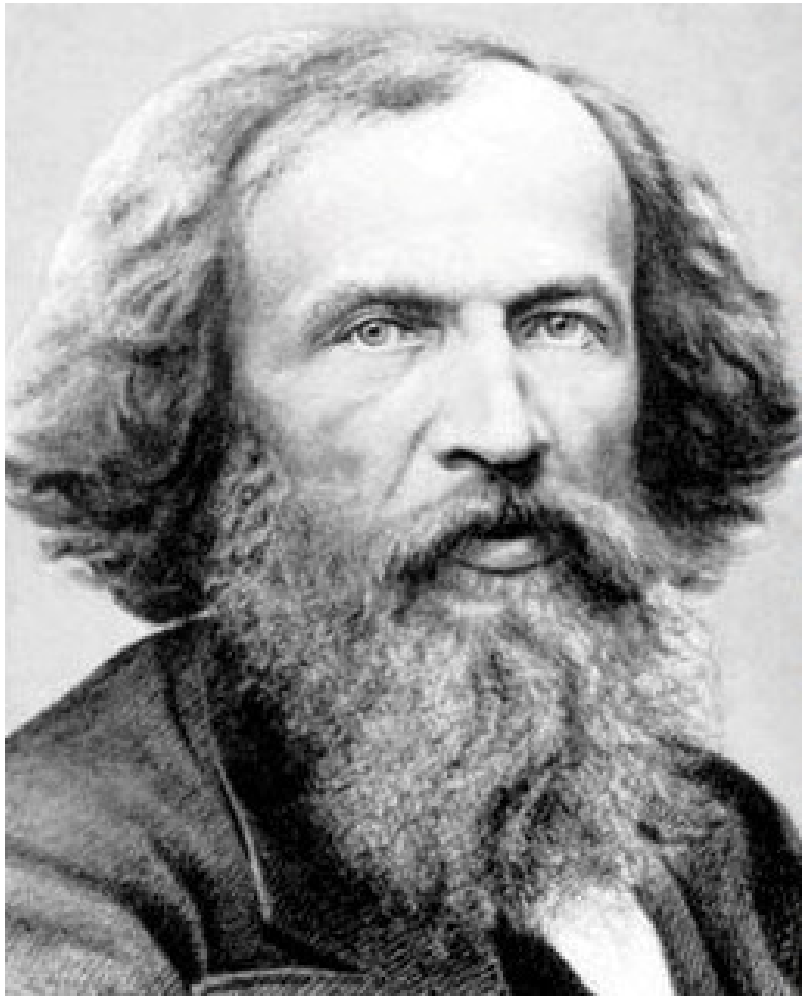
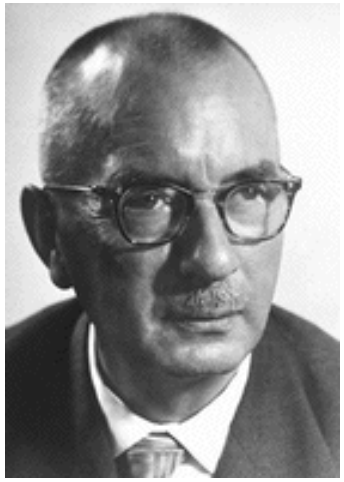


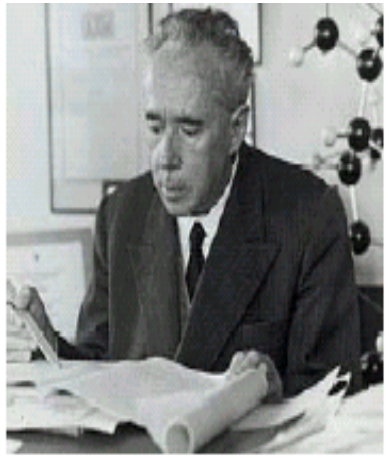
"It is the function of science to discover the existence of a general reign of order in nature and to find the causes governing this order. And this refers in equal measure to the relations of man - social and political - and to the entire universe as a whole."

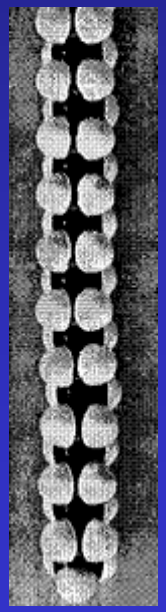
Dmitri Mendeleev

Some profound questions : How many elements can a Periodic Table hold ? Is there a limit ? Can we conceive of a time when the periodicity will be broken or is the Table an axiom of nature ?

METAL CATALYZED OLEFIN POLYMERIZATION







BUNDESREPUBLIK DEUTSCHLAND

AUSGEGEBEN AM 14. APRIL 1960

DEUTSCHES PATENTAMT

PATENTSCHRIFT

Nr. 973 626

KLASSE 39c GRUPPE 25 01

INTERNAT. KLASSE C 08 f

Dr. Dr. e. h. Karl Ziegler, Mülheim/Ruhr,
Dr. Heinz Breil, Oberhausen (Rhld.), Dr. Erhard Holzkamp, Düsseldorf,
und Dr. Heinz Martin, Mülheim/Ruhr
sind als Erfinder genannt worden

Dr. Dr. e. h. Karl Ziegler, Mülheim/Ruhr

Verfahren zur Herstellung von hochmolekularen Polyäthylenen

DE 973626
Nov 18, 1953

CRYSTALLINE HIGH POLYMERS OF α-OLEFINS

Sir:

No crystalline polymers of olefinic hydrocarbons containing asymmetric carbon atoms in the principal chain of the macromolecules have been reported. Such a lack of crystallinity has been explained[1] by considering such polymers as copolymers of two types of random distributed monomeric units, differing only in the configuration of their dissymmetric group.

G.Natta
JACS 77, 1708, 1955
(March 20, 1955)

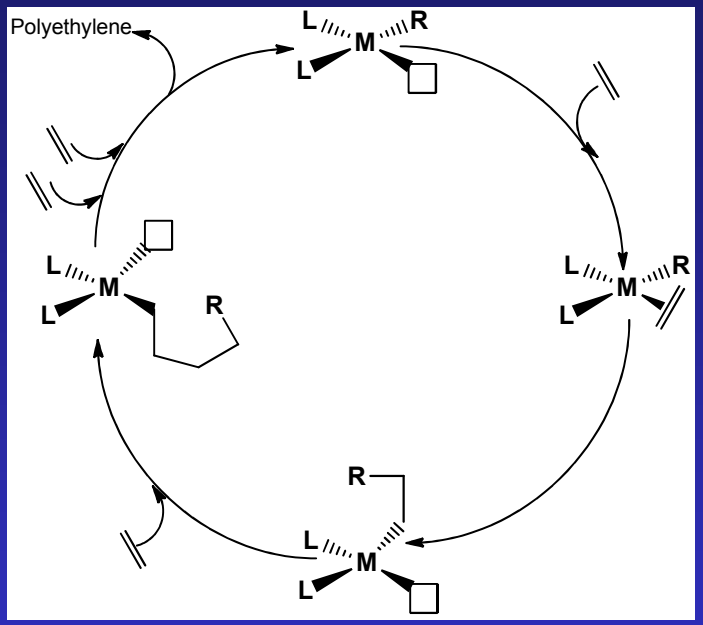
ZIEGLER AND NATTA AWARDED NOBEL PRIZE IN 1963

Citation

For their discovery in the field of chemistry and technology of high polymers

"Nature synthesises many stereoregular polymers (cellulose, rubber, biomacromolecules). This ability has so far been thought to be a monopoly of nature operating with biocatalysts known as enzymes. But Professor Natta has broken this monopoly"

A. Fredga, Nobel Presentations, 1963



Quintessential Chemistry : Formation of Carbon –Carbon Bonds

Since Victor Grignard in 1912 more than ten Noble Prizes in Chemistry have been awarded to chemists who discovered new ways to make carbon-carbon bonds, the latest being Suzuki, Negishi and Heck in 2010

POLYOLEFINS via CATALYSIS INVOLVING METALS AND LIGANDS

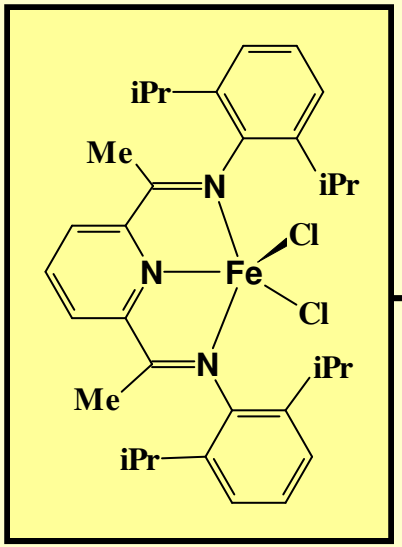
CATALYSTS

- Group 4 (Ti-Mg)
- Group 4 metallocenes
  Ligands, bis Cp, mono Cp, bridged Cp, non Cp
- Group 4 metal complexes
  Bis(salicylaldiimine)
- Group 8 Metal complexes
  Fe(II), bis(imino)pyridine
- Group 10 metal complexes
  Ni(ii) / Pd(ii) α-diimine
  Neutral nickel
- Group 11 metal complexes
  Cu(II) complexes

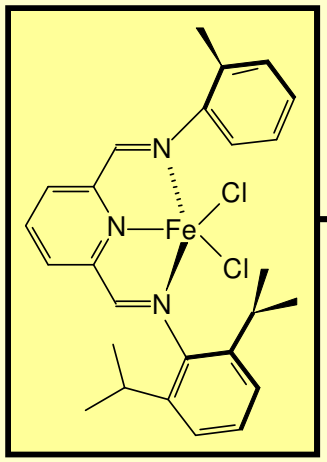
POLYOLEFIN HOMO AND COPOLYMERS

- iPP/Syndio PP
- Elastic PP
- Plastomers
- EPDM's
- Syndio polystyrene
- Ethylene-styrene interpolymers
- Cyclic olefin copolymers
- In-situ branched PE's without comonomers (Versipol, CGC)
- Polar copolymers at ends of branches
- In chain polar olefin copolymers

LATE TRANSITION METAL COMPLEXES FOR OLEFIN POLYMERIZATION

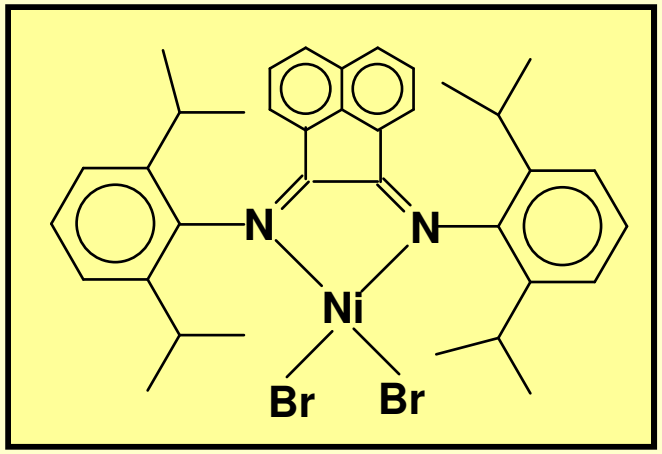


- **Sterically bulky ortho-substituents reduce the rate of β-H tranfer and result in high Mw polyethylene**
- **Chain transfer aluminium alkyl: Broad/Bimodal MWD**

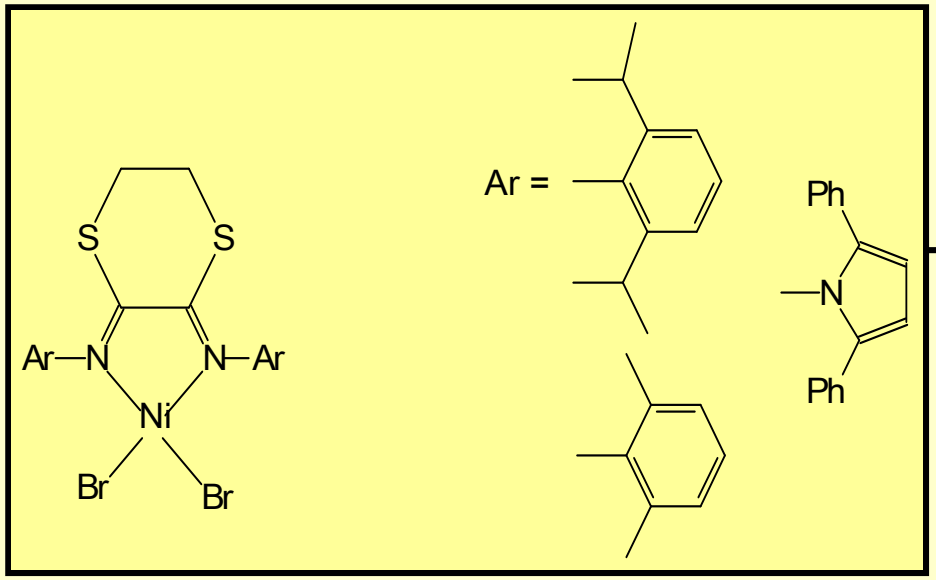


- **C1-symmetric complex**
- **Simultaneous polymerization and oligomerization**
- **Highly crystalline PE**
- **Oligomerization highly selective with 95 % α-olefins**

LATE TRANSITION METAL COMPLEXES FOR OLEFIN POLYMERIZATION

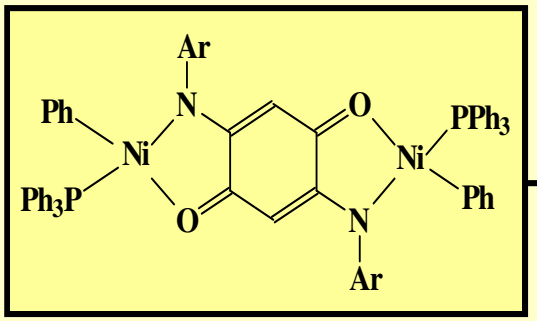


- Polymerize ethylene and α-olefins to high molecular weight polymers
- Linear to branched polymers
- Narrow MWD
- Copolymerization of ethylene with polar monomers

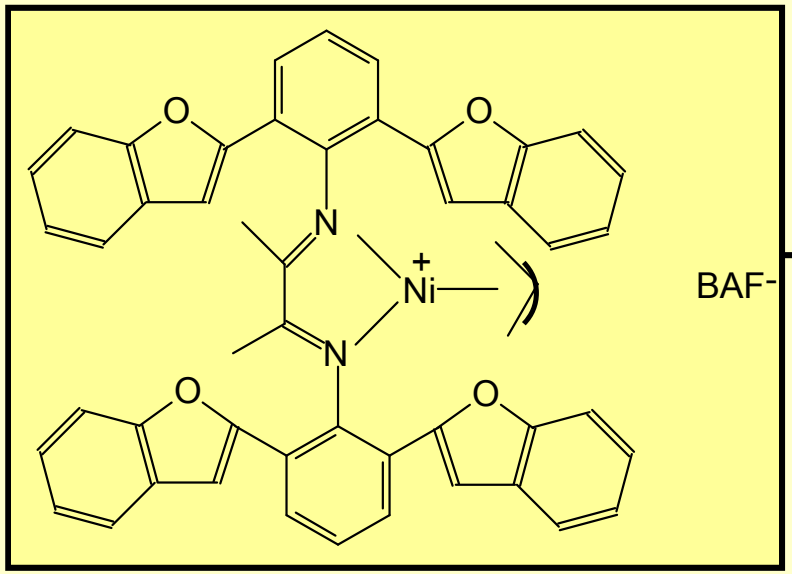


- GAVILAN technology
- Excellent catalyst activity and thermal stability
- Copolymerization of ethylene with cyclic olefins, polar monomers
- Narrow MWD and composition distribution

LATE TRANSITION METAL COMPLEXES FOR OLEFIN POLYMERIZATION

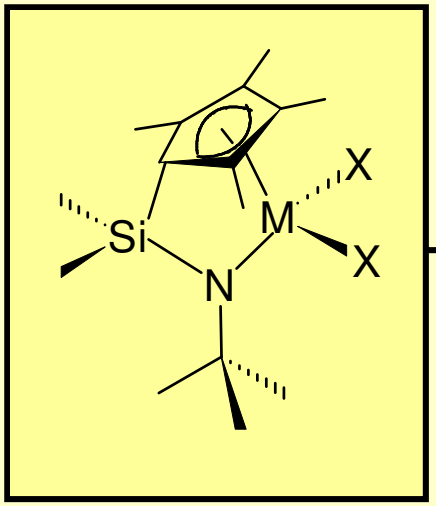


- **Neutral, single-component binuclear catalyst**
- **Moderately branched PE with broad MWD**
- **Presence of more than one active species due to interaction between the metal centers**

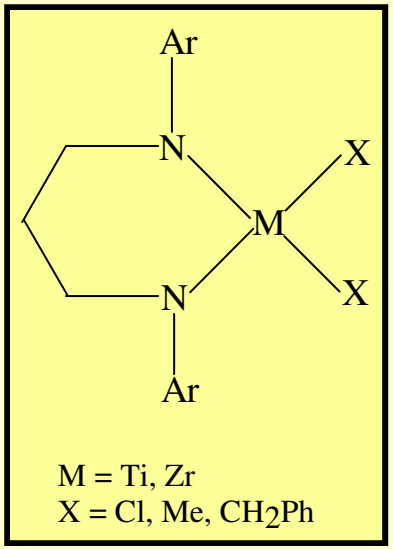


- **High thermal stability ; Catalyst activity retained even at 150°C**
- **Ultrahigh molecular weight PE (Mw > 2.5 million at 70 °C)**

NON-METALLOCENE EARLY TRANSITION METAL CATALYSTS FOR OLEFIN POLYMERIZATION

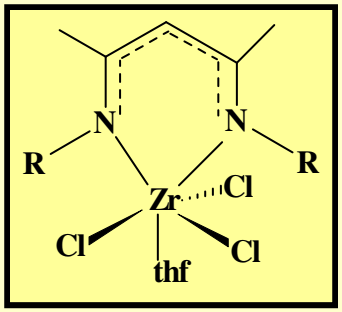


- **Mono-Cp complexes with covalently linked amide donor and a short bridging group**
- **Cp-M-N angle < 115°**
- **Long chain branched PE**
- **Copolymerization of ethylene with α-olefins, styrene, cyclic olefins etc**

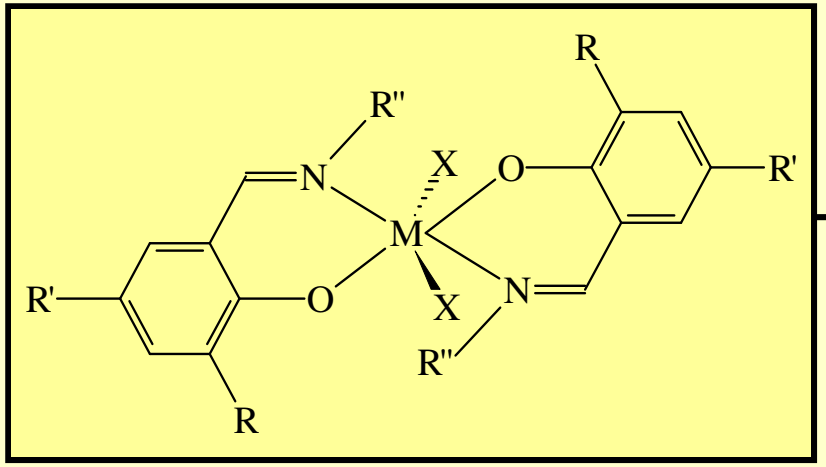


- **Polymerization of higher α-olefins with high activities (>105 g poly(hexene) mmol-1 Ti h-1)**
- **Chain transfer to aluminum in presence of MAO**
- **Living polymerization in presence of B(C6F5)3**

NON-METALLOCENE EARLY TRANSITION METAL CATALYSTS FOR OLEFIN POLYMERIZATION

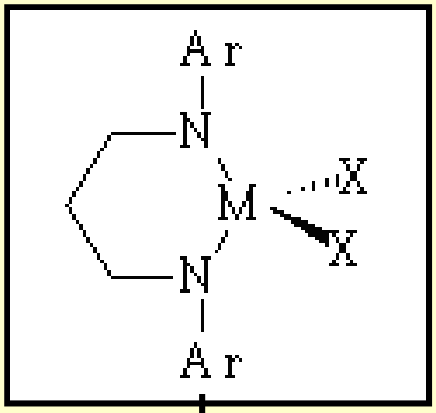


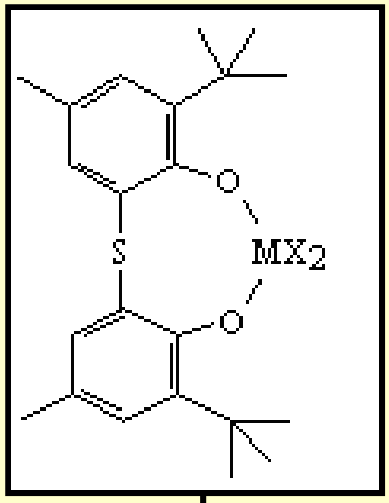
- Very low activities for mono(β-diketiminates)
- Bis(β-diketiminates) exhibit higher activities
- Higher activities when R = p-CF3C6H3

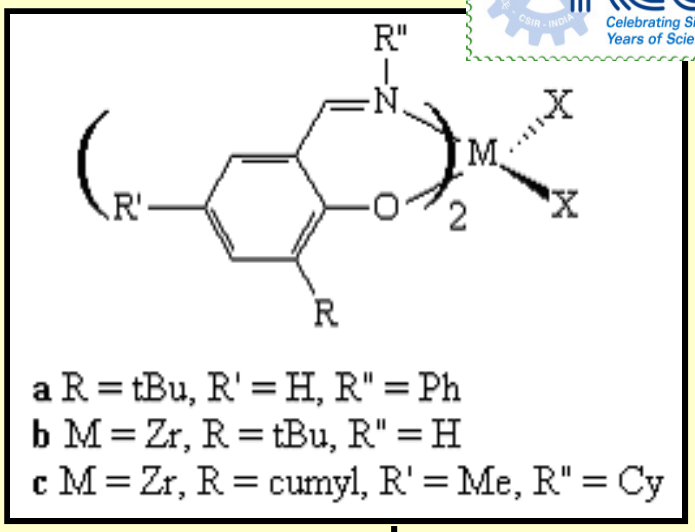


- Very high catalyst activities and polymer molecular weights
- Bulky R" leads to higher Mw
- Bulky R group increases catalyst activity
- Living polymerization: Block copolymers

EARLY TRANSITION METAL CATALYSTS







a R = tBu, R' = H, R" = Ph
b M = Zr, R = tBu, R" = H
c M = Zr, R = cumyl, R' = Me, R" = Cy

Chelating diamide ligands

Active catalyts for hexene-1 polymerization in combination with MAO

A = 350 x10^3 gmmol^{-1} Zr^{-1} h^{-1} bar^{-1} , X = Me, Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$

McConville, D. H. Macromolecules, 1996, 29, 5241.

Chelating phenoxide ligands

Active catalysts for ethylene polymerization with 500 eqv MAO

A = 1580 gmmol^{-1} Ti^{-1} h^{-1} bar^{-1}

van der Linden, A.; Schaverien, C. J. J. Am. Chem. Soc. 1995, 117, 3008.

Salicylaldiminato ligands

Active catalysts for ethylene polymerization

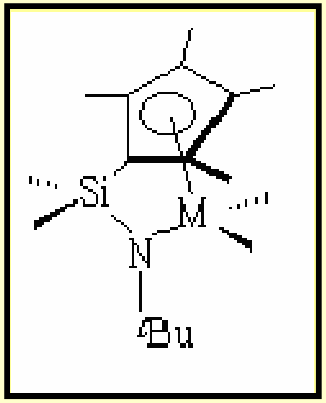
3a. A = 519 x 10^3 gmmol^{-1} Zr^{-1} h^{-1} bar^{-1}

3b. A = 550 x 10^3 g mmol^{-1} Zr^{-1} h^{-1} bar^{-1} R' ' =Ph

3c. A = 43x 10^5 gmmol^{-1} Zr^{-1} h^{-1} bar^{-1}

Fujita, T. J. Am. Chem. Soc. 2001, 123, 6847

MIXED LIGANDS



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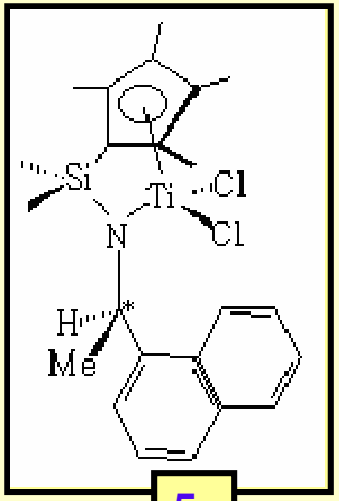

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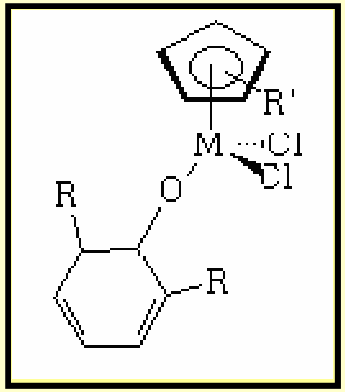

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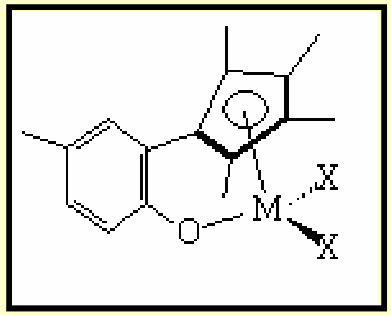


7

Complex 4 is the well kmown constraint geometry catalyst

Complex 5 is an active catalyst for the polymerization of propylene resulting in a PP with 56% isotacticity

Zr complex 6 (R= tBu, R' = Me_5) exhibits an activity of 4260 gmmol^{-1} Zr^{-1} h^{-1} bar^{-1} for the polymerization of ethylene

7/$Ph_3C^+B(C_6F_5)_4^-$ is an active catalyst for ethylene polymerization; A = 2100 gmmol^{-1} Ti^{-1} h^{-1} bar^{-1}

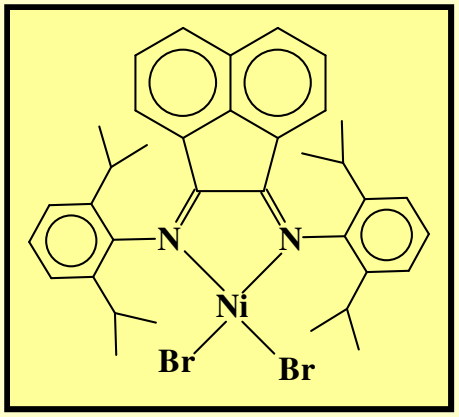
McKnight, A. L.; Waymouth, R. M. Chem. Rev. 1998, 98, 2587.

Fink, G. J. Mol. Catal. A: Chem, 2000, 157, 83.

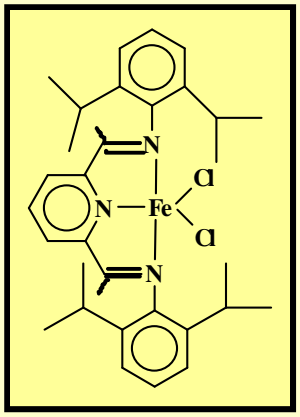
Nomura, K. Organometallics, 1998, 17, 2152.

Marks, T. J. Organometallics, 1997, 16, 5958.

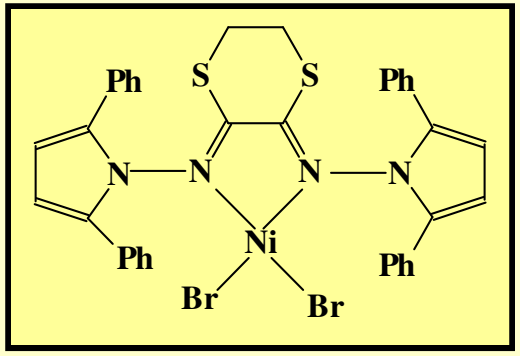
NEWER METALS AND LIGANDS FOR OLEFIN POLYMERIZATION



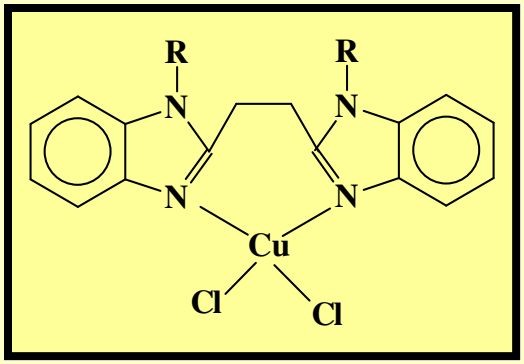
Brookhart(1995)



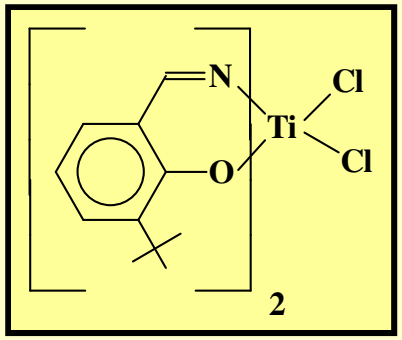
Gibson(1999)



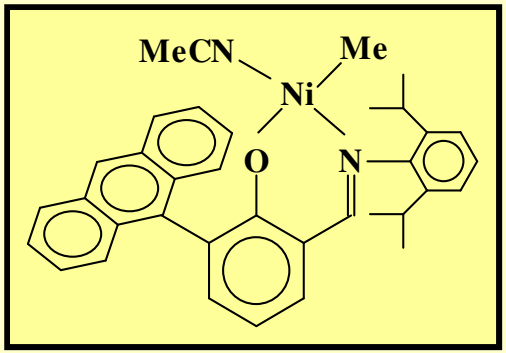
Eastman Chemicals (2000)



Exxon Mobil (2000)



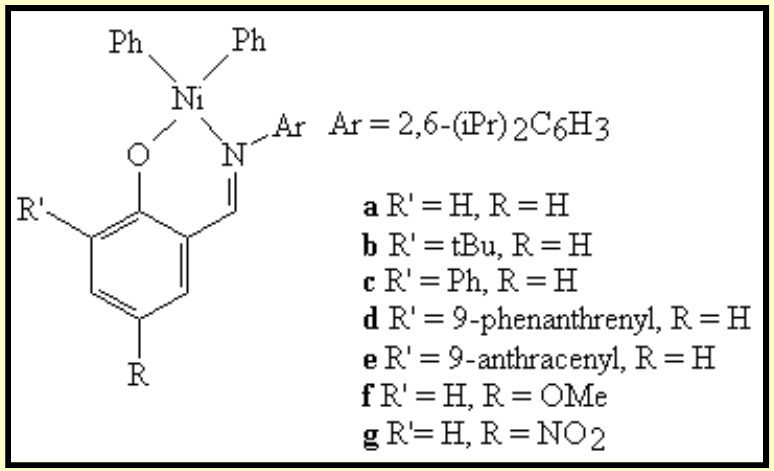
Fujita(2002)



Grubbs(2003)

V.C.Gibson and S.K.Spitzmesser; *Chem.Rev.*, 103, 283-315 (2003)

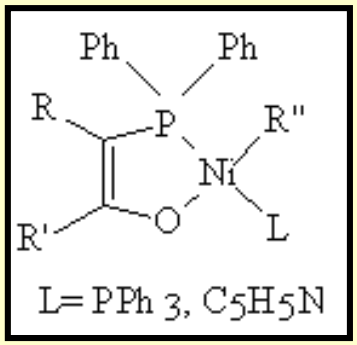
LATE TRANSITION METAL COMPLEXES



N,O donors

Neutral Ni(II) salicyldiminato complexes produce poly(ethylene)s with 30-55 branches/1000 C

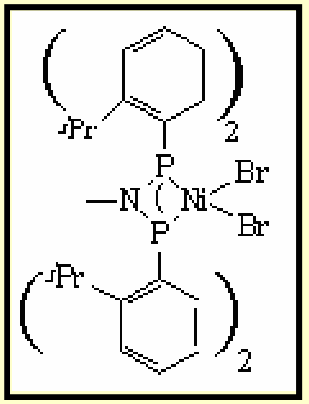
Grubbs, R. H. *Organometallics,* 1998, 17, 3149



P,O donors

Activity of 5300 gmmol^{-1} Ni^{-1} h^{-1} bar^{-1} when R = COOR, R´ = CF_3, C_3F_7 or C_6F_5 for oligomerization of ethylene

Claverie, J. *Macromolecules*, 2001, 34, 2438.

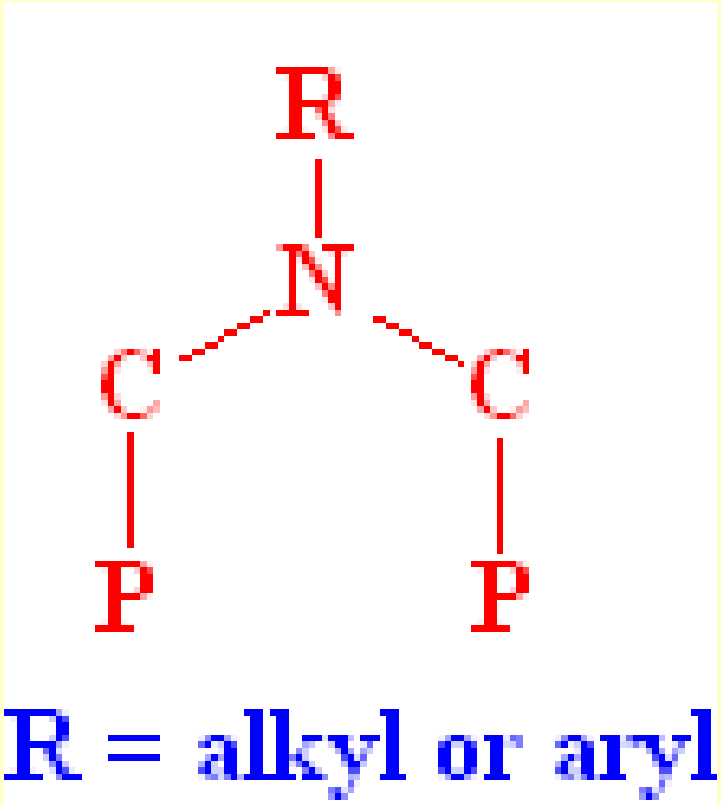


P,P donors

Activity of 2200 gmmol^{-1} Ni^{-1} h^{-1} bar^{-1} resulting in a linear high molecular weight PE

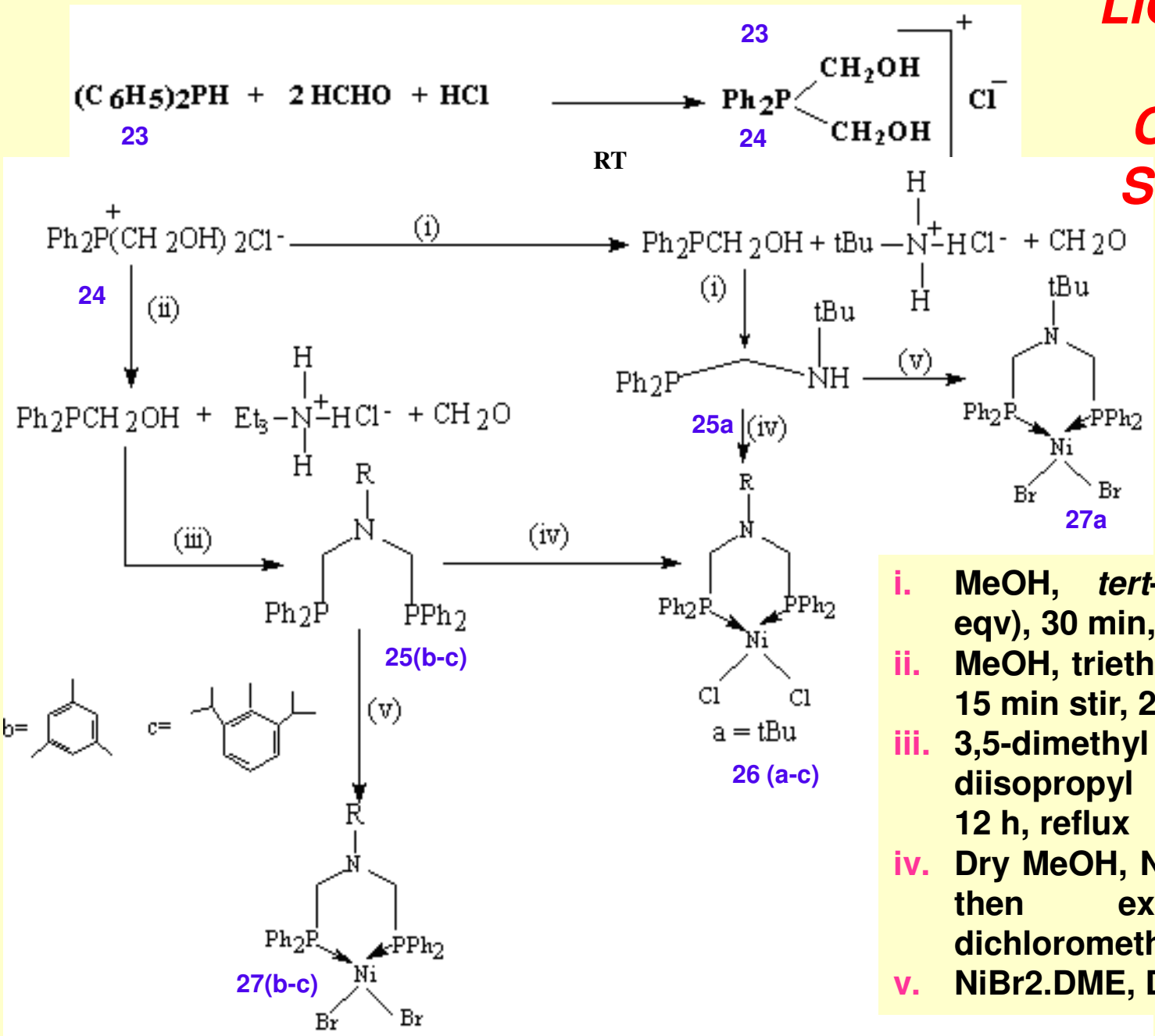
Wass, D.F *Organometallics,* 2001, 20, 4769.

INFLUENCE OF GEOMETRIES OF LIGANDS ON THE COURSE OF POLYMERIZATION



- **Catalyst activity depends upon the nature of the metal and the ligand environment (steric and electronic)**
- **Bi-dentate ligands have a preference for a specific geometry which can be probed using the concept of "bite angle", donor atom – metal – donor atom angle**
- **Examine P-C-N-C-P framework: Isolate electronic effects from steric effects**

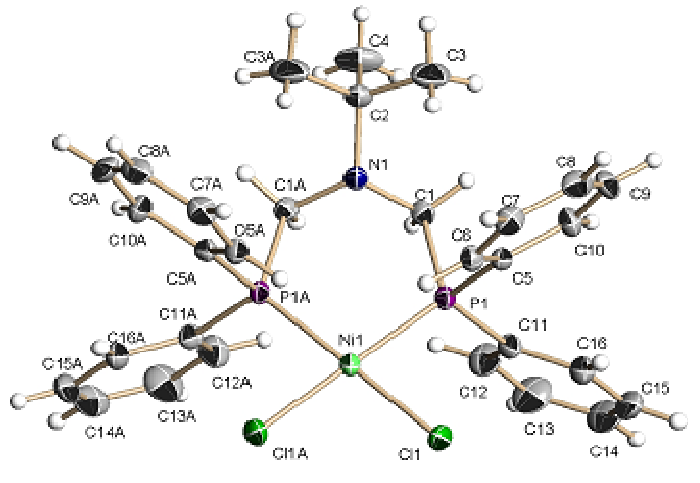
LIGAND AND METAL COMPLEX SYNTHESIS



i. MeOH, *tert*-butyl amine (7 eqv), 30 min, 25°C
ii. MeOH, triethylamine (1.3 eqv), 15 min stir, 25°C
iii. 3,5-dimethyl aniline/2,6-diisopropyl aniline (0.5 eqv), 12 h, reflux
iv. Dry MeOH, NiCl2, reflux, 24 h, then extraction with dichloromethane
v. NiBr2.DME, DCM, 25°C, 24 h

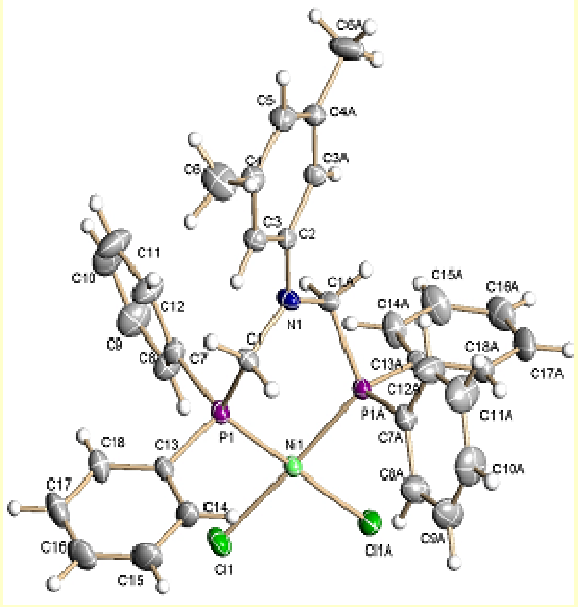
BITE ANGLE INFLUENCES SELECTIVITY

Ethylene 1 atm



A
N- t-Butyl
X : Cl
Bite Angle : 89.7

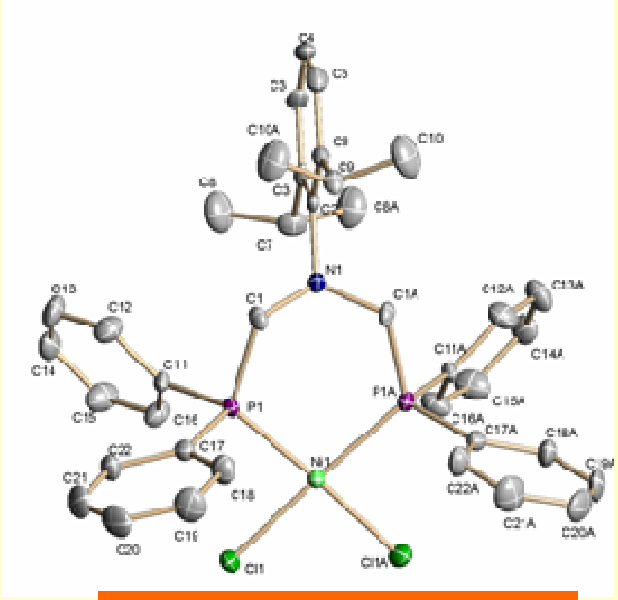
TOF : 2177
Butene-1 : Hexene-1
91 : 9



B
N-3,5-dimethyl phenyl
X : Cl
Bite Angle : 96⁉

TOF : 3699
Butene-1 : Hexene-1
70: 30

ETHYLENE POLYMERIZATION AT 5 ATM



C
N-2,6-disopropyl
X : Cl
Bite Angle : 97.2

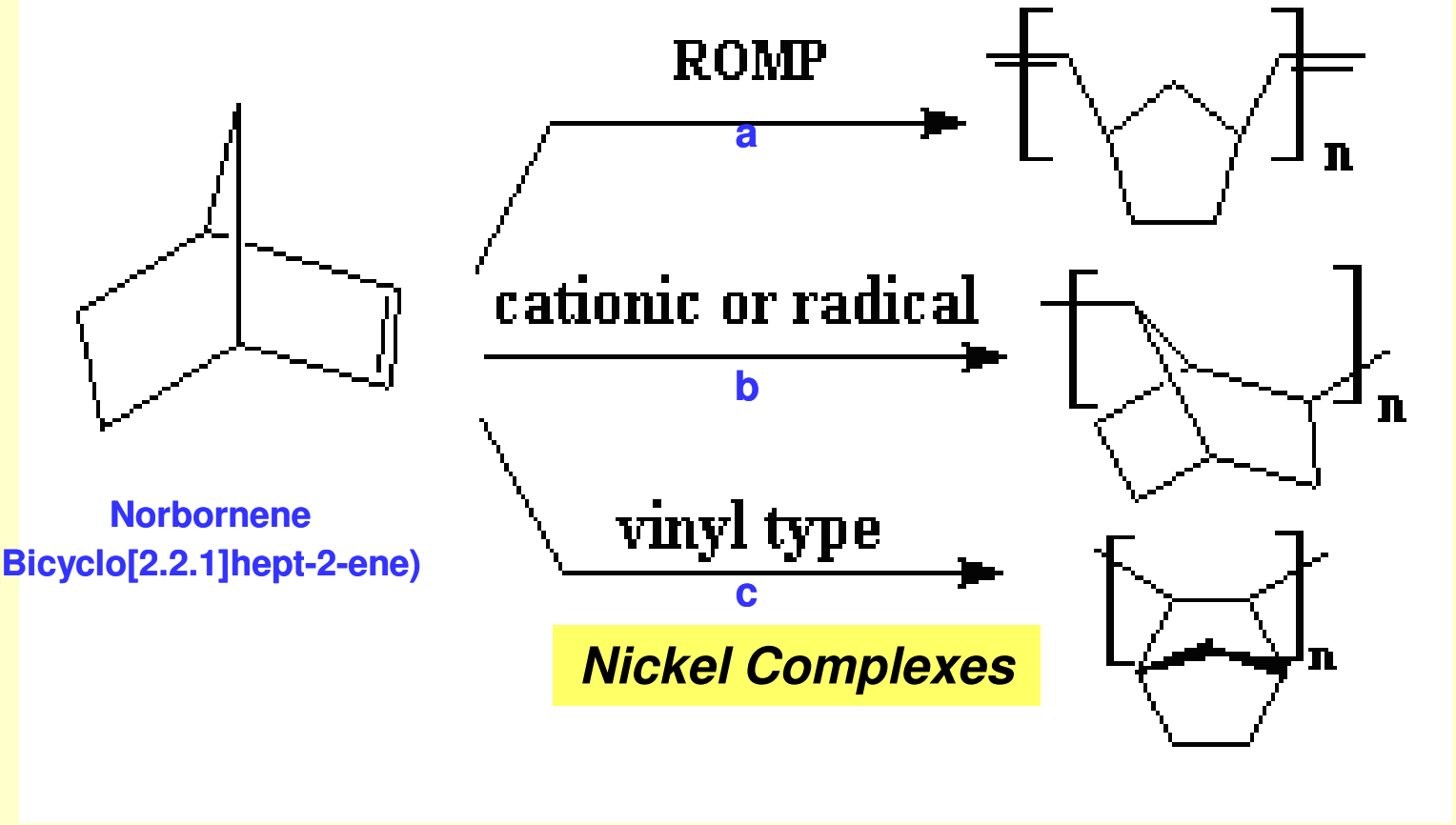
A : Mw 190,000; Tm 130 ° C; 2 ethyl branches per 1000C atoms; predominantly linear

B : Mw 155,000; Tm 118 ° C 6 ethyl branches per 1000 C atoms

C : No Polymerization
Only Butene-1 : Hexene-1 in the ratio of 94 :6

A : N-t-Butyl : Lower bite angle and larger steric shielding from both sides
B : N- 3,5-dimethyl phenyl : Larger bite angle and lesser steric shielding
C : N-2,6-di-isopropyl : Total steric shielding of the metal center

POLYMERIZATION OF NORBORNENE

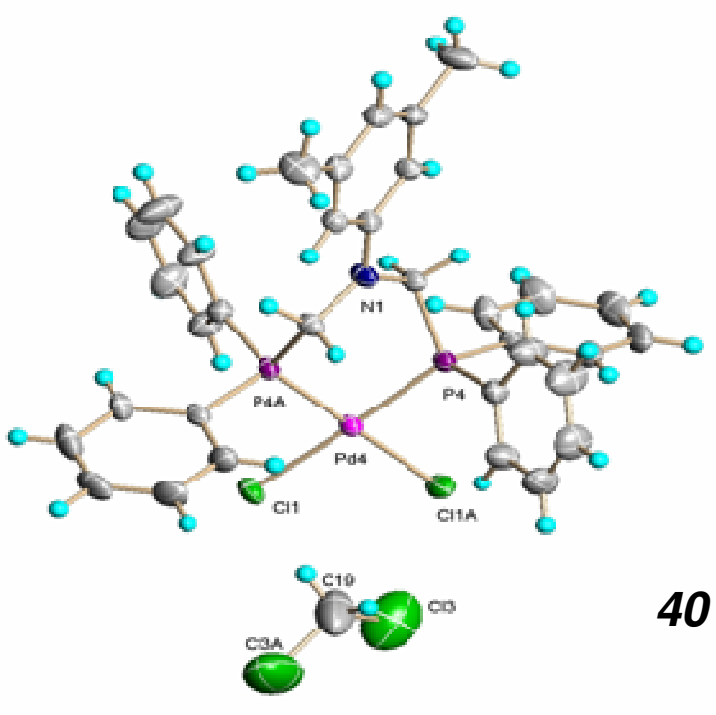


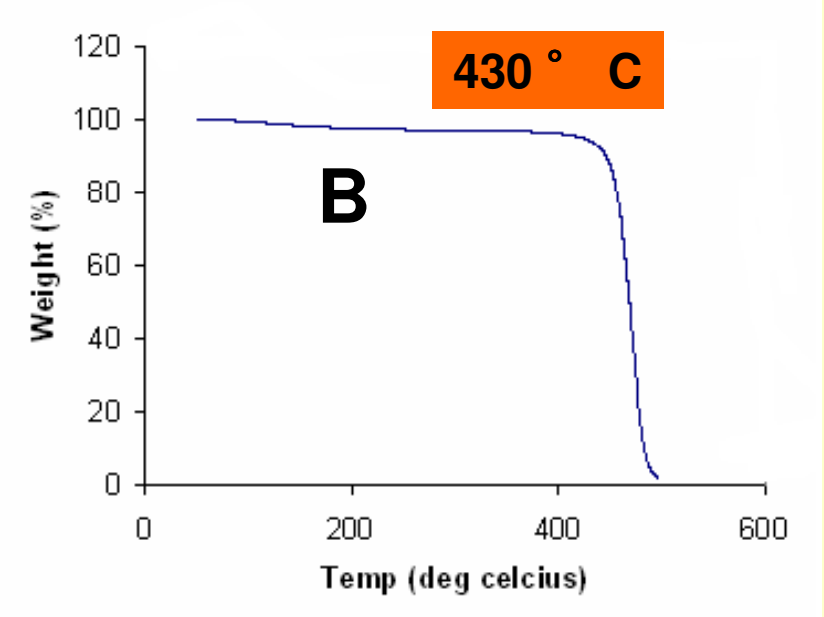
Not easy to polymerize ; requires open coordination sites on metal centers

POLYMERIZATION OF NORBORNENE

(co-catalyst : Tris (pentafluorophenyl) borane

- A : Poly(norbornene) , 40 % conversion; Mw : 770,000
- B : Poly(norbornene) , 70 % conversion, Mw 500,000
- C : No polymerization



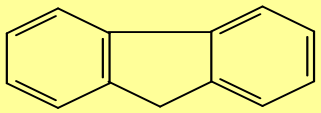


N; 3,5-dimethyl, X; Cl, M : Pd
40 % conversion; polymer insoluble in common solvents

POLYMERIZATION OF ETHYLENE USING ansa - η5 - MONOFLUORENYL COMPLEXES OF GROUP 4 METALS

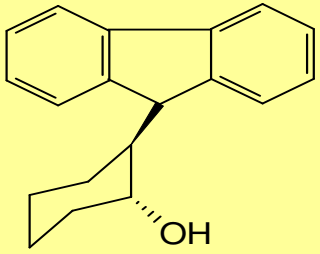
A. Rajesh and S. Sivaram, Polymer Bulletin, 2011

SYNTHESIS GROUP 4 METAL COMPLEXES OF TRANS-2-[9-(H) FLUORENYL] CYCLOHEXANOL



1

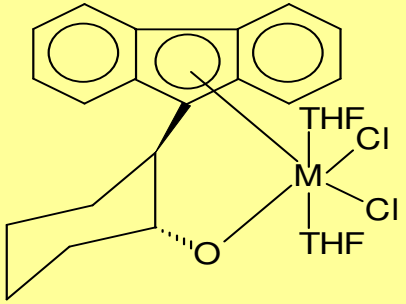
(a) n-BuLi, Et_2O, -20°C
(b)  , Et_2O; -20°C -30°C
(c) aq.NH_4Cl



2

(a) n-BuLi, THF, -78°C
(b) $MCl_4(thf)_2$, THF, -78°C
reflux, 6h

- ***Metal – oxygen bond on reactivity***
- ***Axial-equatorial geometry***
- ***Fluxtional properties of the cyclohexane ring***
- ***Open structure; easy access of monomer to metal center***



3

3a M = Ti
3b M = Zr
3c M = Hf

POLYMERIZATION OF ETHYLENE AT 5 BAR: NATURE OF METAL

Toluene(30 mL); MAO; Al/M: 2000; PC2H4: 5 bar; time: 1 h

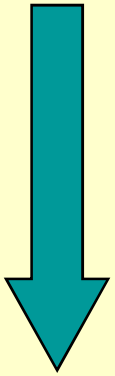
Complex	Complex (μmol)	Tp (°C)	Yield (g)	Activity g PE $mmo^{l-1}M.h^{-1}$	$[\eta]^b$ dL/g	Mw ($x10^4$)	M_w/M_n	Tm (°C
3a (Ti)	19.0	25	0.20	10	5.2	n.d	n.d	142
3b(Zr)	17.6	25	1.0	57	5.1	n.d	n.d	134
3c(Hf)	15.5	25	0.04	2.6	2.8	n.d	n.d	133
3a(Ti)	19.0	80	0.30	16	2.5	n.d	n.d	140
3b(Zr)	17.6	80	3.7	210	0.9	12.2	BM	122
3c(Hf)	15.5	80	0.07	4.5	2.0	n.d	n.d	134

[b] measured in decahydronaphthalene at 135°C

- Lower catalyst activity of hafnium complex 3c when compared to 3a and 3b can be attributed to stronger Hf-C bond which slows down monomer insertion and chain propagation
- Titanium and zirconium complexes produce poly(ethylene)s in the ultra high molecular weight range
- Titanium complex 3a resulted in poly(ethylene)s with exceptionally high crystalline melting point

ANALYSIS OF FRACTION A

Tp (°C)	[η] dL/g	Mw (x10^4)	Mw/Mn	Tm (°C)
25	5.1	n.d	n.d	132
40	4.7	n.d	n.d	130
60	1.04	n.d	n.d	125
80	0.93	12.2	Bimodal	121
100	0.59	7.7	Bimodal	123



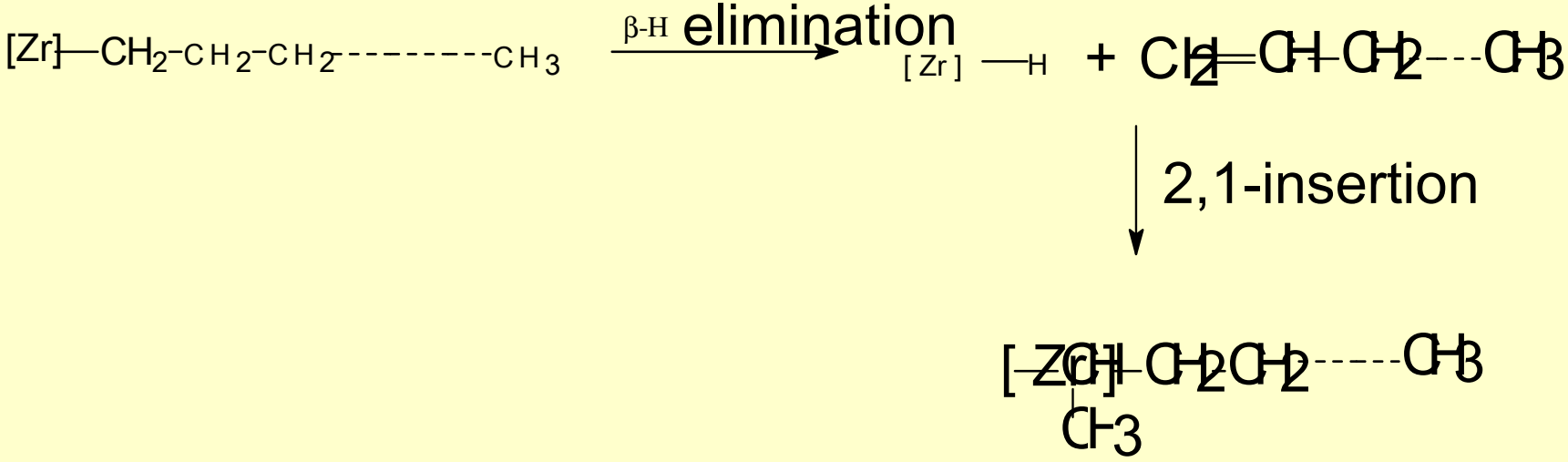
- Progressive decrease in crystalline melting point (Tm) with increasing temperature indicates increase in degree of branching
- Bimodal molecular weight distribution implies the presence of more than one active center

NATURE OF BRANCHING AND BRANCHING DISTRIBUTION OF FRACTION A OBTAINED USING 3b / MAO

Temp.	Total branching/1000 C	Branching with respect to total	
		Methyl (%)	Long chain (%)
25	0	0	0
40	0	0	0
60	0.7	0	100
80	1.4	0	100
100	2.6	60	40

- **Formation of methyl branches in addition to long chain branches at 100°C**

MECHANISM FOR THE FORMATION OF METHYL BRANCHES



- **Methyl branches result from β-H elimination followed by 2,1-insertion of the α-olefin into the [Zr – H] species (Regio-errors)**
- **2,1-insertion favored at higher temperatures**

SUMMARY

- **Titanium complex 3a at 25° C produce ultra high molecular weight poly(ethylene)s with unusually high crystalline melting point. This indicates that the PE is defect free and linear with methyl terminal chain ends**
- **Zirconium complex 3b at 25° C also produce ultra high molecular weight poly(ethylene)s; however, the crystalline melting points are lower, similar to conventional HDPE**
- **Zr complex 3b exhibits activity even at 100°C. The thermal stability of the catalyst system can be attributed to the metal-oxygen bond in the complex**

SUMMARY

- **The solid poly(ethylene)s consists of exclusively long chain branches (> 6 carbons) at 60 and 80°C, whereas, at 100°C, methyl branches are also observed in addition to long chain branches**
- **Long chain branches are formed as a result of β-H transfer reaction followed by reincorporation of the resulting long chain α-olefin (macromonomers of ethylene)into the growing polymer chains**
- **Methyl branches result from β-H elimination followed by 2,1-insertion of the α-olefin into the [Zr]-H centers , (Regio- errors). This reaction is favored at 100° C**
- **Bimodal MWD observed at higher temperatures indicate the presence of at least two active centers, one capable of selective oligomerization and the other capable of either homo-polymerization or copolymerization of ethylene with higher α-olefins**

SUMMARY

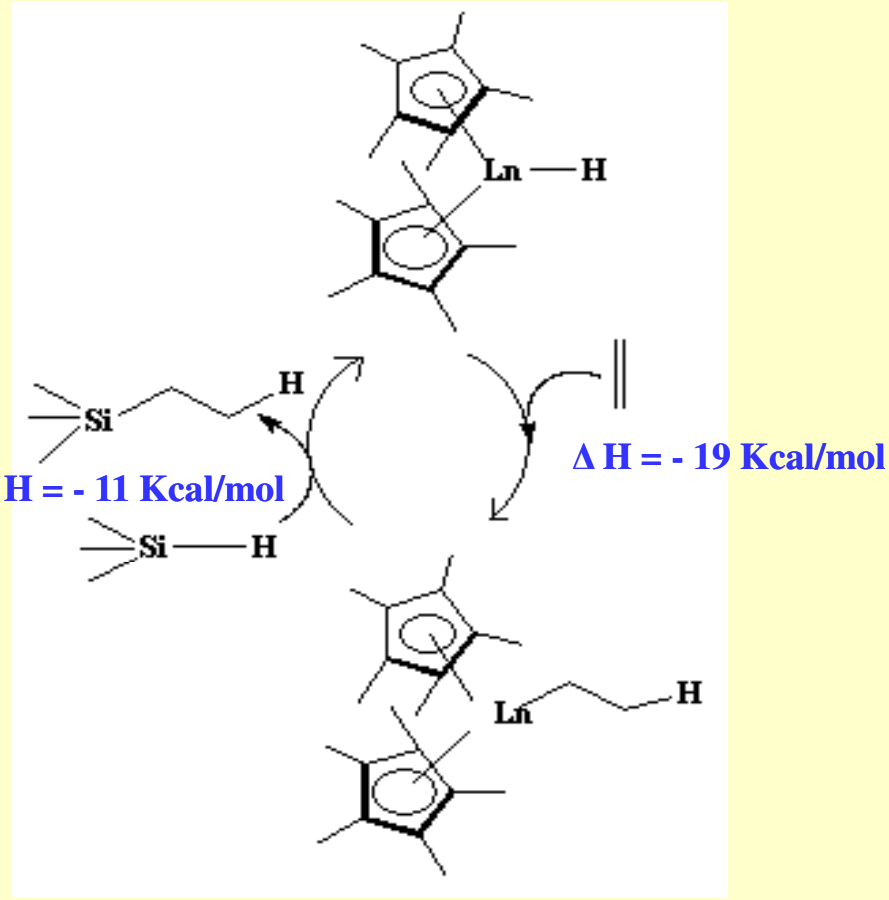
- **First example of a single zirconium complex that exhibits such diverse polymerization behavior producing a range of poly(ethylene) s from linear high molecular weight to lower molecular weight polymers with short and long chain branching as well as single site as well dual site behavior**

- **This behavior can be tuned only with one variable, namely, temperature of polymerization**

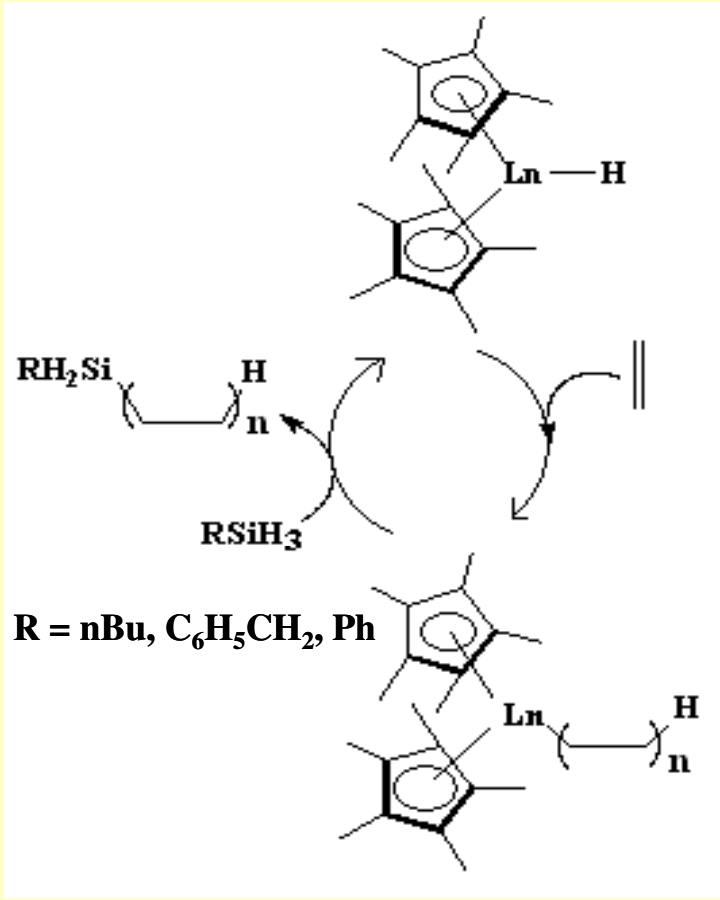
- **The Cp - Zr – O bite angle increases with temperature due to the increased conformational mobility of the cyclohexane at higher temperatures, resulting in β-H elimination, reinsertion and 2,1- insertion.**

SILANOLYTIC CHAIN TRANSFER IN ETHYLENE POLYMERIZATION USING BIS[N(3-TERT-BUTYL SALICYLIDENE) 2,3,4,5,6-PENTAFLUOROANILINATO] Ti (IV) DICHLORIDE

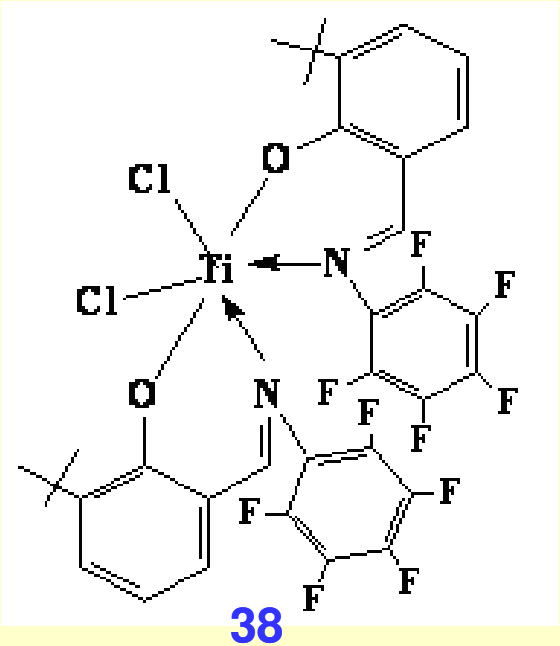
Amrita Chaki , to be published



Organolanthanide catalyzed olefin hydrosilylation



Formation of silyl-capped poly(olefin)s



38

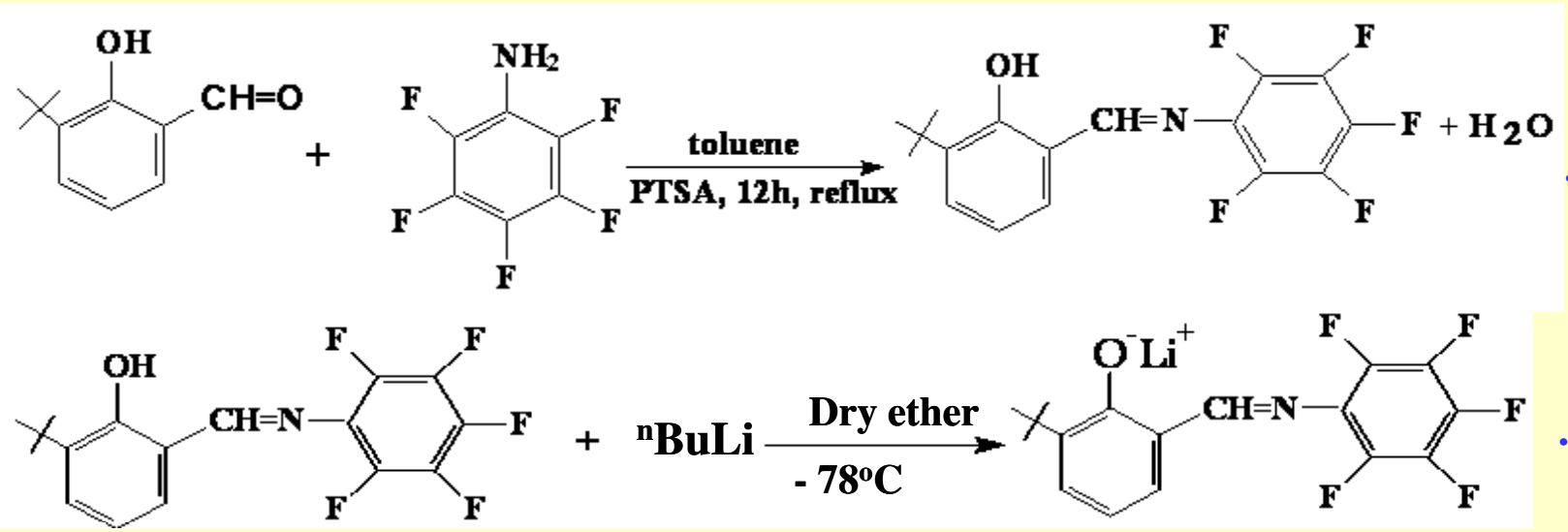
BIS(PHENOXYIMINE) TITANIUM (IV) COMPLEX

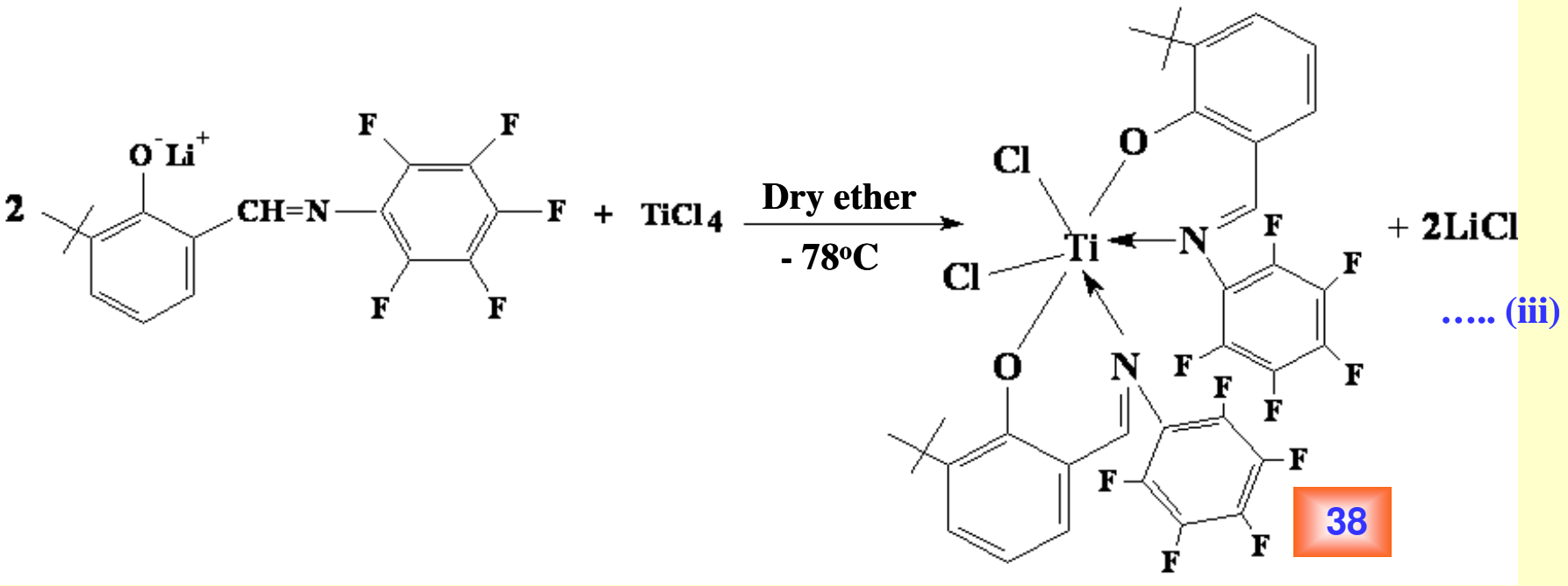
- **Exhibit high activity (A = 34000 gmmol^{-1} Ti^{-1} h^{-1} bar^{-1}) for the homo-polymerization of ethylene**
- **A linear relationship between Mn and polymerization time ; exhibits some characteristics of "living" behavior**

Objective

Examine the feasibility of organo- titanium mediated chain transfer to silanes

SYNTHESIS OF BIS [N(3-TERT BUTYL SALICYLIDENE)2,3,4,5,6-PENTAFLUOROANILINATO] TI (IV) DICHLORIDE (38):

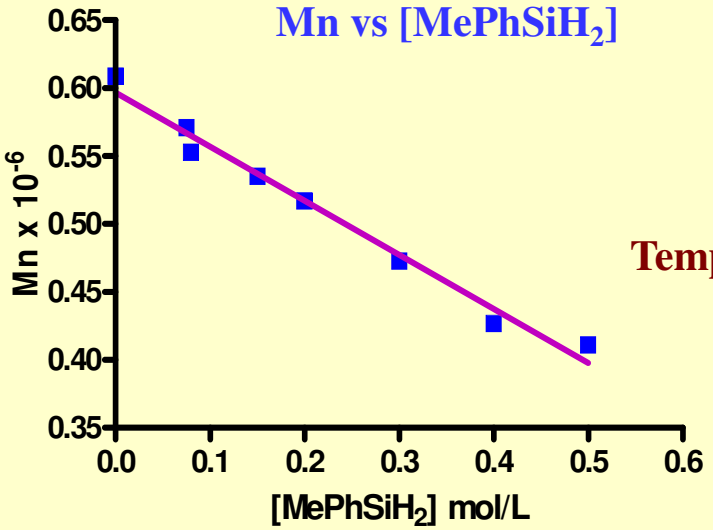


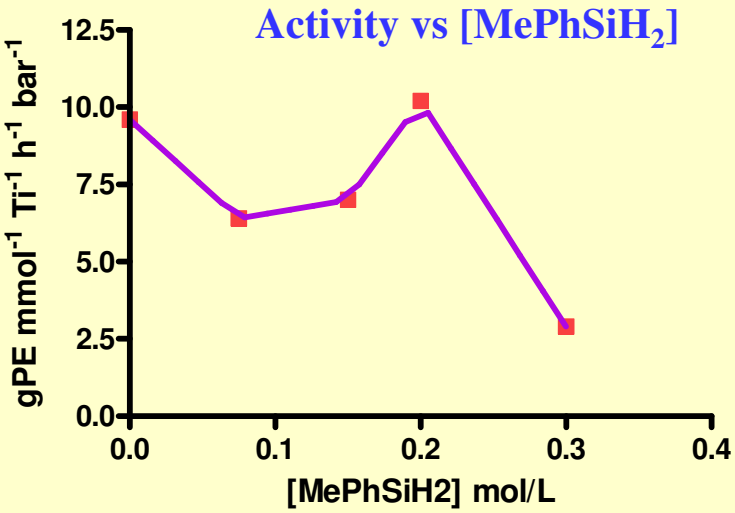


$MePhSiH_2$ as chain transfer agent

Entry	$MePhSiH_2$ M	Yield (g)	[b]Activity X 10^{-3}	[c]Mn x 10^{-6}	[c]Mw x 10^{-6}	[c]PDI
1	0	0.240	9.6	0.60	1.10	1.8
2	0.075	0.160	6.4	0.57	1.08	1.9
3	0.15	0.175	7.0	0.54	0.97	1.8
4	0.20	0.255	10.2	0.52	0.93	1.8
5	0.30	0.073	2.9	0.47	0.87	1.8

[a] Conditions: PC_2H_4 = 1.013 bar, time = 3 min, [Ti] = 0.5 µmol, Al/Ti = 2500, [b] gPE $mmol^{-1}$ Ti^{-1} h^{-1} bar^{-1} [c] GPC studies in trichlorobenzene at 135°C





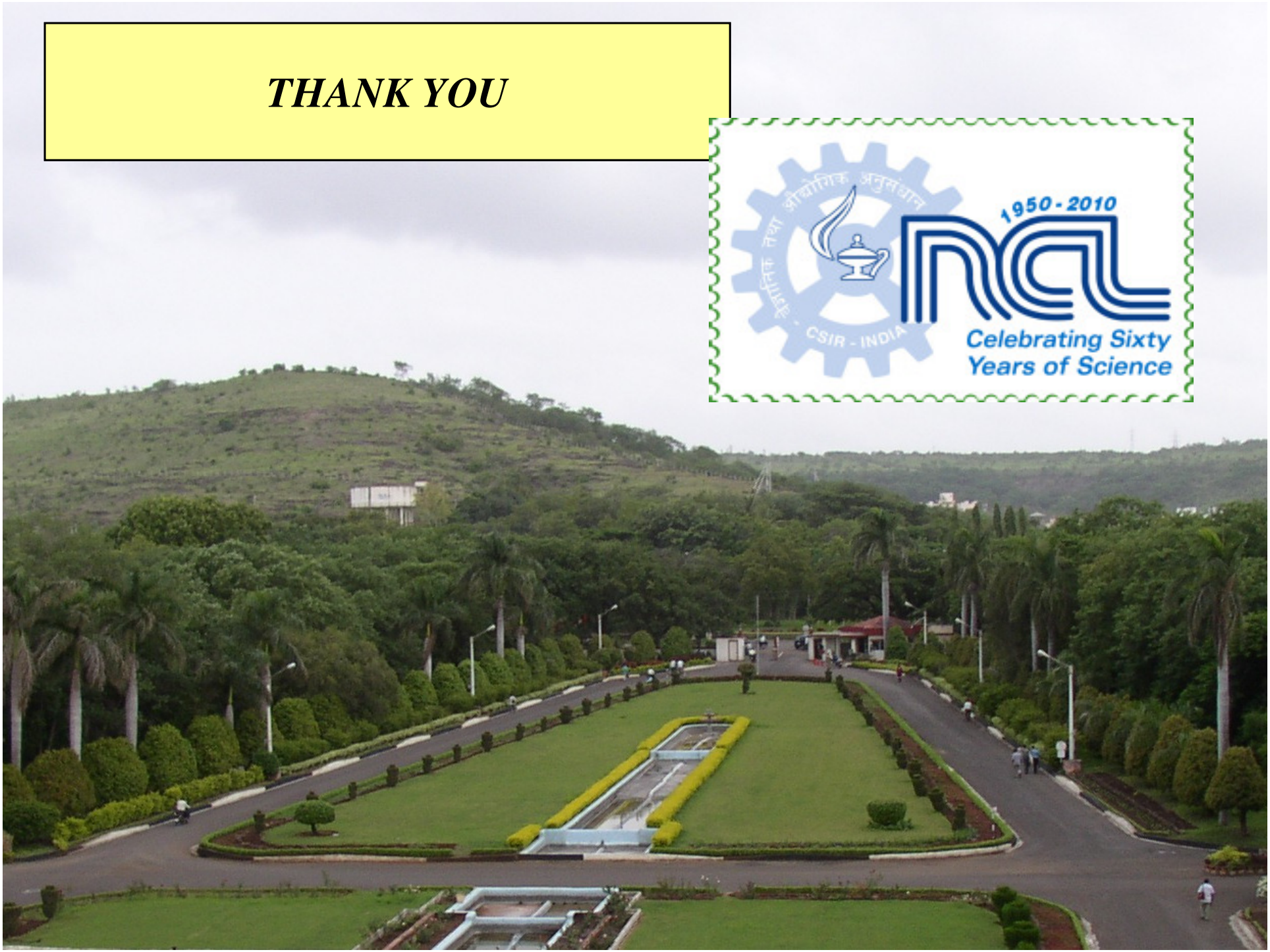
COMPARISON OF CHAIN TRANSFER CONSTANT VALUES

Catalyst	Silane	Temp (°C)	Cs
38	$PhSiH_3$	25	102
38	$PhSiH_3$	0	54
38	$PhSiH_3$	-10	45
38	$MePhSiH_2$	0	59
[a] $[Me_2Si(Me_4C_5)^tBuN]TiMe^+B(C_6F_5)_4^-$	$PhSiH_3$	25	35
$Me_2Si(Me_4C_5)_2SmCH(SiMe_3)_2$	$PhSiH_3$	25	130

[a] propylene polymerization

Silanes are effective chain transfer agents with open framework Titanium catalysts

THANK YOU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