Design of Novel Group 4 *ansa*-Metallocene Compounds and their Role as Catalysts in the Polymerization of Olefins

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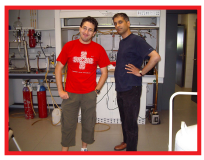

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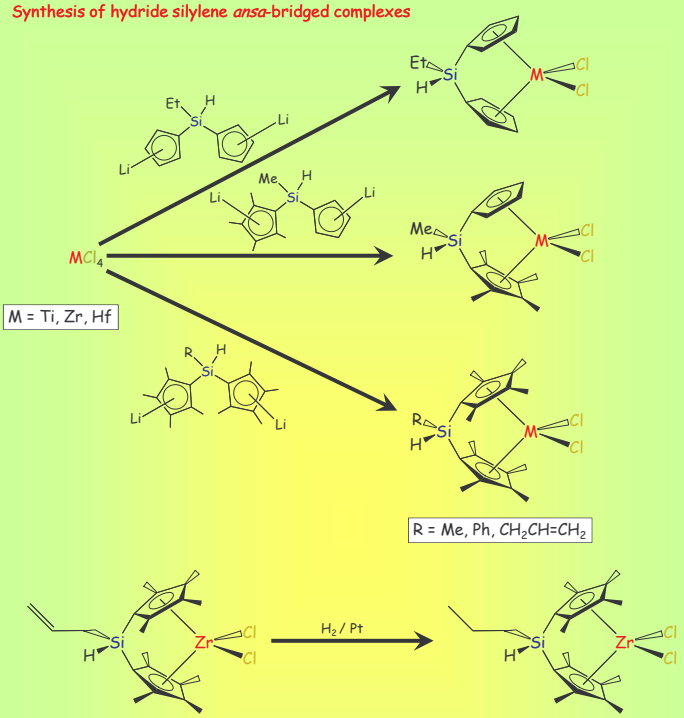
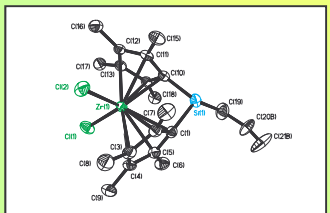
Introduction

Since the discovery by Sinn and Kaminsky that zirconocene complexes in the presence of MAO were able to polymerize olefins there has been a dramatic expansion in this field. One of the main focuses of this research is centred on the tailoring of metallocene complexes that can direct the catalytic reaction in producing polymers with desired physical properties. Ligand design is therefore of utmost importance in the development of "made to measure" single-site olefin polymerization catalysts. In addition the introduction of functional groups in the ligand system can be later exploited in immobilizing the catalyst on different substrates.

Synthesis of hydride silylene *ansa*-bridged complexes





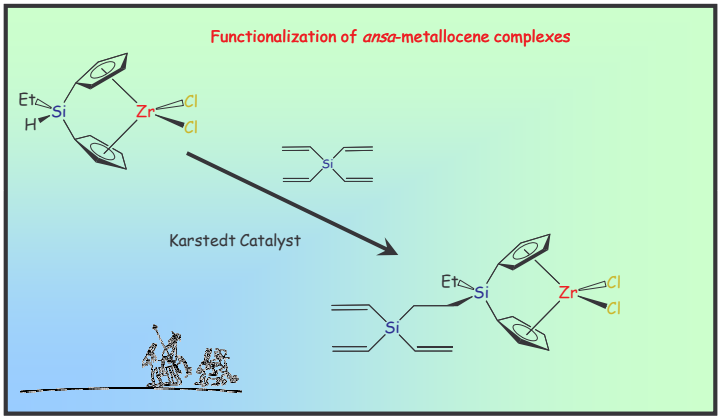
Molecular structure of $[Zr\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_9Me_4)_2\}Cl_2]$

Ethylene Polymerization Results[a]

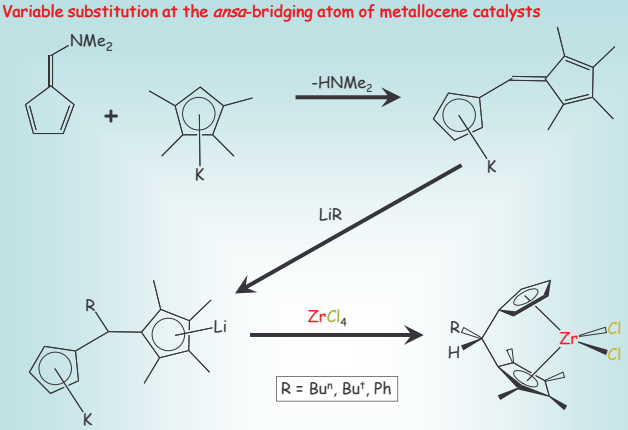
Catalyst	Activity [b]
$[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$	24600
$[Zr\{Et(H)Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$	11100
$[Zr\{Me(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$	9633
$[Zr\{Me(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$	26407
$[Zr\{Ph(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$	15967
$[Zr\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$	6373
$[Zr\{CH_3CH_2CH_2(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$	18633

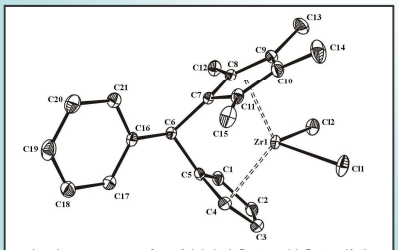
[a] At 20 °C, 2 bar monomer pressure, 200 mL toluene, $[Al] = 9 \times 10^{-2}$ mol L^{-1}, $[Zr] = 3 \times 10^{-5}$ mol L^{-1}, $t_{Pol} = 15$ min.
[b] In kg Pol (mol Zr.h)$^{-1}$

Functionalization of *ansa*-metallocene complexes



Variable substitution at the *ansa*-bridging atom of metallocene catalysts





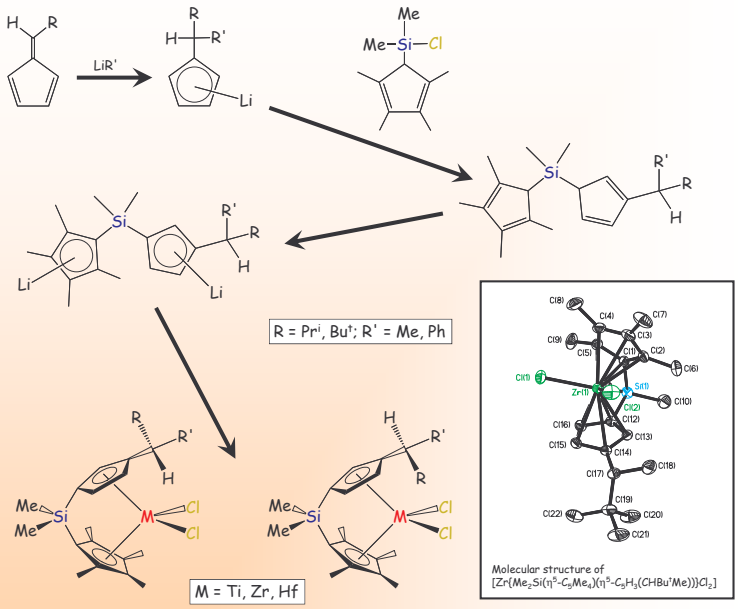
Molecular structure of $[Zr\{Ph(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$

Ethylene Polymerization Results[a]

Catalyst	Activity [b]
$[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$	1713
$[Zr\{Ph(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$	2107
$[Zr\{Bu^t(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$	653
$[Zr\{Bu^n(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$	7347

[a] At 20 °C, 2 bar monomer pressure, 200 mL toluene, $[Al] = 3 \times 10^{-2}$ mol L^{-1}, $[Zr] = 3 \times 10^{-5}$ mol L^{-1}, $t_{Pol} = 15$ min.
[b] In kg Pol (mol Zr.h)$^{-1}$

The great majority of isospecific metallocene catalysts have a C_{2v} symmetry. The inconvenience is caused by the synthesis producing a mixture of the catalytically stereoselective *rac*- and non stereoselective *meso*-isomers. C_1 symmetric catalysts however do not suffer this problem and by finely tuning the steric conditions isotactic polypropylene can be produced.



Molecular structure of $[Zr\{Me_2Si(\eta^5\text{-}C_9Me_4)(\eta^5\text{-}C_5H_3(CHBu^tMe))\}Cl_2]$

Ethylene Polymerization Results[a]

Catalyst	Activity [b]
$[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$	1713
$[Zr\{Me_2Si(\eta^5\text{-}C_9Me_4)(\eta^5\text{-}C_5H_3(CHBu^tMe))\}Cl_2]$	4720
$[Zr\{Me_2Si(\eta^5\text{-}C_9Me_4)(\eta^5\text{-}C_5H_3(CHPr^iMe))\}Cl_2]$	1367
$[Zr\{Me_2Si(\eta^5\text{-}C_9Me_4)(\eta^5\text{-}C_5H_3(CHBu^tPh))\}Cl_2]$	1233
$[Zr\{Me_2Si(\eta^5\text{-}C_9Me_4)(\eta^5\text{-}C_5H_3(CHPr^iPh))\}Cl_2]$	1500

[a] At 20 °C, 2 bar monomer pressure, 200 mL toluene, $[Al] = 3 \times 10^{-2}$ mol L^{-1}, $[Zr] = 3 \times 10^{-5}$ mol L^{-1}, $t_{Pol} = 15$ min.
[b] In kg Pol (mol Zr.h)$^{-1}$

Propylene Polymerization Results[a]

Catalyst	Activity [b]	*mmmm* %
$[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$	557	atactic
$[Zr\{Me_2Si(\eta^5\text{-}C_9Me_4)(\eta^5\text{-}C_5H_3(CHBu^tMe))\}Cl_2]$	317	84
$[Zr\{Me_2Si(\eta^5\text{-}C_9Me_4)(\eta^5\text{-}C_5H_3(CHPr^iMe))\}Cl_2]$	550	86
$[Zr\{Me_2Si(\eta^5\text{-}C_9Me_4)(\eta^5\text{-}C_5H_3(CHBu^tPh))\}Cl_2]$	217	89
$[Zr\{Me_2Si(\eta^5\text{-}C_9Me_4)(\eta^5\text{-}C_5H_3(CHPr^iPh))\}Cl_2]$	350	86

[a] At 20 °C, 2 bar monomer pressure, 200 mL toluene, $[Al] = 3 \times 10^{-2}$ mol L^{-1}, $[Zr] = 3 \times 10^{-5}$ mol L^{-1}, $t_{Pol} = 15$ min.
[b] In kg Pol (mol Zr.h)$^{-1}$