Hydrosilylation in the Design and Functionalization of *ansa*-Metallocene Olefin Polymerization Catalysts

Santiago Gómez-Ruiz, Sanjiv Prashar, Mariano Fajardo, Antonio Antiñolo, Antonio Otero

Dpto. de Tecnología Química, Ambiental y de los Materiales, E.S.C.E.T., Universidad Rey Juan Carlos, 28933, Móstoles, (Madrid). Spain. E-mail: s.gomez@escet.urjc.es
Dpto. de Química Inorgánica, Orgánica y Bioquímica. Facultad de Químicas, Universidad de Castilla-La Mancha, 13071, Ciudad Real, Spain.

Introduction

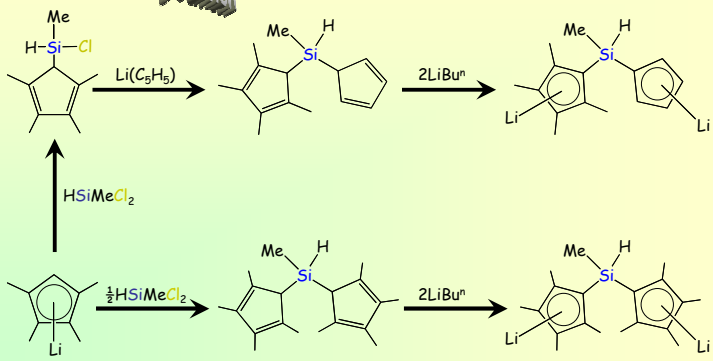
The discovery by Sinn and Kaminsky of the catalytic activity of group 4 metallocene compounds in the polymerization of olefins has led to a rapid and ongoing development in this area. The principal efforts in this research field are centred on the design of metallocene catalysts capable of originating materials with "user defined" physical properties.

The current trend in the field of metallocene catalysis is moving towards supported catalysts that allow homogeneous single-site selectivity in a heterogeneous medium. The introduction of functional groups in the ligand system can be exploited in immobilizing the catalyst on different substrates without greatly altering the general structure of the metallocene complex.

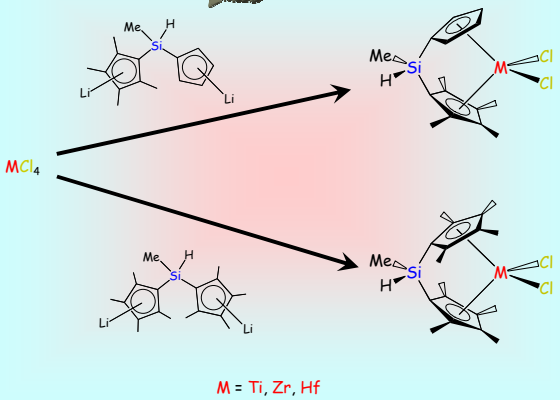
As a continuation of our previous work related to single-site catalysts, we report the synthesis of new group 4 *ansa*-metallocene complexes and the reactivity of the *ansa*-bridge Si-H bond in its hydrosilylation of unsaturated silanes.

The modification of the *ansa*-metallocene systems via hydrosilylation processes opens up the possibility of supporting the single-site catalysts on silane substrates such as vinyl functionalized silica or dendrimeric systems.

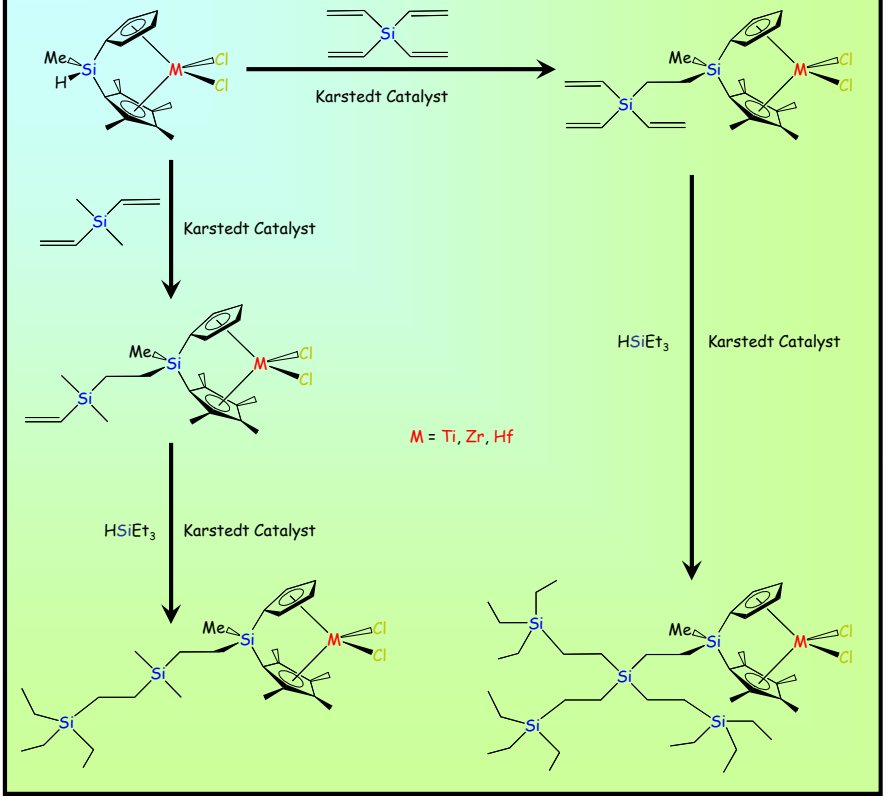
Ligand Preparation

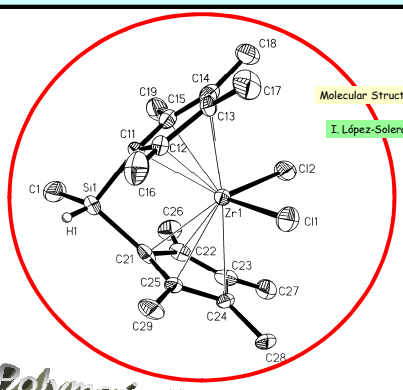


ansa-Metallocene Synthesis



Hydrosilylation



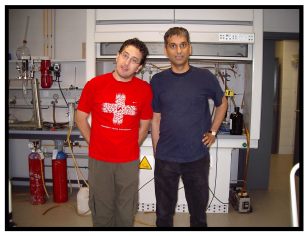


Polymerization

Ethylene Polymerization Results[a]

Catalyst	Activity [b]	M_w (g mol^{-1})	M_w/M_n
[Zr(η5-C5H5)2Cl2]	24600	200000	5.5
[Zr{Me(H)Si(η5-C5Me4)(η5-C5H4)}Cl2]	9633	169200	3.3
[Zr{Me(H)Si(η5-C5Me4)2}Cl2]	26407	151300	3.6
[Zr{(CH2=CH)3SiCH2CH2(Me)Si(η5-C5Me4)(η5-C5H4)}Cl2]	13352	273000	3.9
[Zr{Me2(CH2=CH)SiCH2CH2(Me)Si(η5-C5Me4)(η5-C5H4)}Cl2]	17907	210100	3.7
[Zr{(Et3SiCH2CH2)3SiCH2CH2(Me)Si(η5-C5Me4)(η5-C5H4)}Cl2]	3907	743300	4.2
[Zr{Me2(Et3SiCH2CH2)SiCH2CH2(Me)Si(η5-C5Me4)(η5-C5H4)}Cl2]	11100	341200	5.0
[Zr{Me2Si(η5-C5Me4)(η5-C5H4)Cl2]	16073	175500	3.2
[Zr{Me2Si(η5-C5H4)2}Cl2]	11500	332800	3.9

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



Propylene Polymerization Results [a,c]

Catalyst	Activity [b]	M_w (g mol^{-1})	M_w/M_n
[Zr(η5-C5H5)2Cl2]	4920	205200	13.1
[Zr{Me(H)Si(η5-C5Me4)(η5-C5H4)}Cl2]	2167	178000	10.7
[Zr{Me(H)Si(η5-C5Me4)2}Cl2]	1967	186000	10.8
[Zr{(CH2=CH)3SiCH2CH2(Me)Si(η5-C5Me4)(η5-C5H4)}Cl2]	1275	193500	10.4
[Zr{Me2(CH2=CH)SiCH2CH2(Me)Si(η5-C5Me4)(η5-C5H4)}Cl2]	1330	176700	9.8
[Zr{(Et3SiCH2CH2)3SiCH2CH2(Me)Si(η5-C5Me4)(η5-C5H4)}Cl2]	1057	300400	11.2
[Zr{Me2(Et3SiCH2CH2)SiCH2CH2(Me)Si(η5-C5Me4)(η5-C5H4)}Cl2]	1250	182400	10.9
[Zr{Me2Si(η5-C5Me4)(η5-C5H4)Cl2]	1567	201300	13.9
[Zr{Me2Si(η5-C5H4)2}Cl2]	1317	183000	12.2

[a] At 20 °C, 2.5 bar monomer pressure, 200 mL toluene, [Al] = 9 × 10^{-2} mol L^{-1}, [Zr] = 3 × 10^{-5} mol L^{-1}, t_{Pol} = 30 min.
[b] In kg Pol (mol Zr.h)$^{-1}$
[c] ^{13}C NMR spectra showed essentially atactic polymers