From Zirconium to Titanium: The Effect of the Metal in Propylene Polymerisation Using *Fluxional* Unbridged Bicyclic Catalysts

Eleonora Polo,[*1] *Simona Losio,*[2] *Fabrizio Fortini,*[2] *Paolo Locatelli,*[2] *Maria Carmela Sacchi*[2]

[1] C.N.R., I.S.O.F. sez. Ferrara, c/o Dip. di Chimica dell'Università di Ferrara, via L. Borsari 46, 44100 Ferrara, Italy
E-mail: tr3@unife.it; Fax: +39 0532240709
[2] C.N.R., ISMAC, via E. Bassini 15, 20133 Milano, Italy
E-mail: m-c.sacchi@ismac.cnr.it; Fax: +39 022362946

Summary: Catalytic systems based on unbridged substituted indenyl systems are becoming of interest in the production of elastomeric polypropylene. A full understanding of the structural features necessary to control this kind of behaviour has not yet been achieved, since relatively slight changes in the molecular architecture can lead to polymers with remarkably different properties.

We report here our recent findings regarding the study of bicyclic zirconium and titanium complexes as fluxional catalysts in propylene polymerisation. Most of them have been synthesised according to a synthetic procedure that allowed us to prepare a series of complexes in which the ring fused to the cyclopentadienyl moiety is saturated and of different sizes, thus introducing a flexibility parameter that can be finely tuned.

The results obtained show that the stereoselectivity induced by this class of catalysts strongly depends both on the structure of the ligand and on the nature of metal atom (Zr *vs.* Ti). The titanium-based catalysts yield polypropylenes with new and interesting microstructures, in particular when an higher stability is achieved through a careful choice of the substitution pattern of the ligands.

Keywords: DSC; fluxional catalysts; metallocene catalysts; NMR; polypropylene

Introduction

Catalytic systems based on unbridged substituted indenyl systems are becoming more and more of interest in the production of elastomeric polypropylene. The possibility of preparing this kind of polymer by means of a single catalyst was introduced by the work of Waymouth and Coates in 1995.[1] They used for the first time the concept of "fluxional" catalysts to describe unbridged metallocenes which are able to interconvert between chiral and achiral rotational isomers on the time scale of the polymerisation reactions. This mechanism accounts

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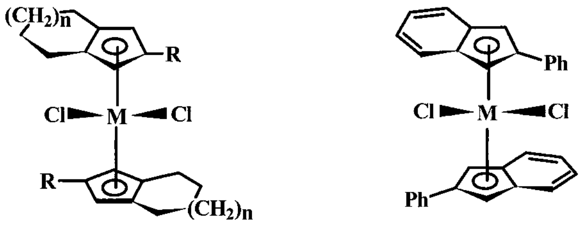
for the isotactic/atactic stereoblock structure obtained, which imparts interesting elastomeric properties to the propylene homopolymer. By a careful choice of the substitution pattern and/or the reaction conditions (temperature, pressure, solvent) it is possible to modulate the isomers interconversion speed in order to achieve the desired stereochemical control. Despite the number of papers appeared in the last years,[2] a clear structure/performance correlation is still lacking and there are several open questions.[3] This is due to the fact that even relatively slight changes in the catalyst molecular architecture are enough to disrupt the delicate balance of the rotational isomers ratio and to produce polymers with remarkably different properties.

In particular, the activity of bicyclic metallocenes, where the ring fused to the cyclopentadienyl unit is saturated, has not yet fully explored[2d] in the field of fluxional catalysts due to the lack of a general synthetic pathway. The study of these metallocenes can be very interesting, since, besides their higher stability and resistance to hydrolysis, they introduce a conformational flexibility parameter that can be finely tuned. Several attempts to synthesise this type of ligands have been reported.[4] However the overall yields were often low or the method used was of limited applicability. Recently, we have reported a new synthetic pathway[5] that has proved successful for a versatile and "tuned" synthesis of tetrahydroindenyl systems and of related ligands containing seven- and eight-membered saturated rings condensed to the cyclopentadienyl moiety. These ligands and their corresponding organometallic compounds have been synthesised in good yields, with only minor purification steps, and the entire procedure is reproducible in large-scale quantities.

We have applied this synthetic method to prepare some series of zirconium complexes[6] and the titanium analogues of the most promising zirconium catalysts (Scheme 1).

Although several zirconium and hafnium complexes have been already studied as fluxional catalysts, very little is known about the behaviour of the corresponding titanium derivatives. It is known that the substitution of zirconium for hafnium yields complexes that are isostructural with the original zirconium catalysts, but which produce polypropylenes of lower isotacticity.[2f] Since the titanium centre allows a closer interaction between the two bent cyclopentadienyl moieties, the effect of the substituents should be enhanced and could affect the interconversion speed between aspecific and isospecific isomers, thus favouring the formation of longer isotactic blocks.



M= Ti, R= -Ph; n = 2 **(2c Ti)**

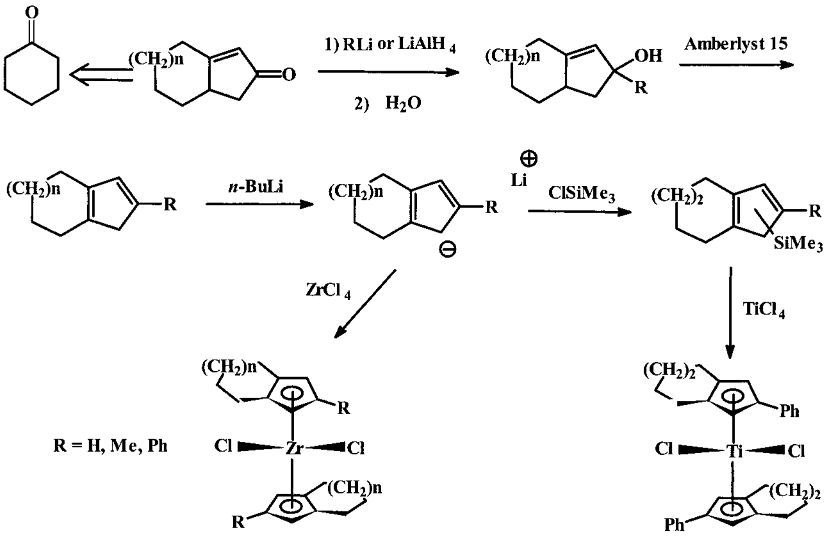
M= Zr R= -H; n= 1-3 **(1a-c)**
R= -Me; n= 1-3 **(2a-c)**
R= -Ph; n= 1-3 **(3a-c)**

M= Ti **(w- 4 Ti)**
M= Zr **(w-4)**

Scheme 1

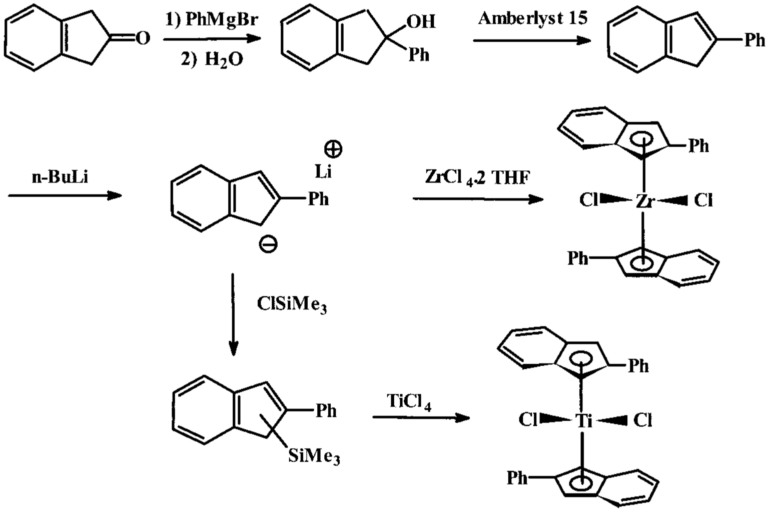
Synthesis of the Complexes

Three series of unbridged bicyclic complexes, containing a six, seven-, or eight-membered saturated ring fused to the cyclopentadienyl unit, and bearing different substituents (-H, $-CH_3$, -Ph) in position 2, were synthesised according to a new synthetic pathway (Scheme 2).



Scheme 2

We have also prepared the catalyst reported by Waymouth, (**w-4**),[1] and its corresponding titanium, (**w-4 Ti**), derivative (Scheme 3). These two catalysts have been used as a reference point under the same polymerisation conditions.



Scheme 3

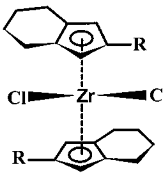
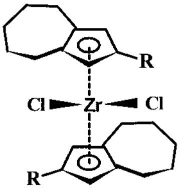
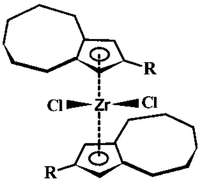
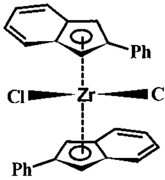
Polymerisation Studies

Zirconium-Based Catalysts

First of all we have studied the polymerisation of propylene at several temperatures (Table 1) using catalysts belonging to three complete series of bicyclic cyclopentadienyl zirconium complexes bearing different substituents (-H, $-CH_3$, -Ph) in position 2; methylaluminoxane (MAO) was used as co-catalyst. All the new catalysts proved to be active and most of the polymers obtained were fully atactic when the polymerisations were performed at 30 °C, while they became partially isotactic at lower temperatures, with an isotactic pentad content [*mmmm*] ranging from 11% to 21%.

The conformation of the saturated ring is likely to play an important role in determining the stereochemical control and/or the rate of interconversion between isospecific and aspecific states. In fact the ^{13}C NMR analysis shows that only when a seven-membered ring is associated with a phenyl substituent in position 2 (**2-c**) the pattern of the spectrum (Figure 1L b) is similar to that of the sample produced with Waymouth's catalyst (Figure 1L a); in this

Table 1. Results of propylene polymerisation with different bicyclic zirconium catalysts[(a)]

Catalyst		**T (°C)**	**Activity**[(b)]	[*mmmm*] [(c)] **(%)**	**Mw (*10^{-3})**	**Mw/Mn**
	R= H **1-a**	30	1172	4.8	27.1	3.1
		0	1000	11.0	25.6	3.0
		-20	1200	11.4	70.2	6.4
	R = CH_3 **1-b**	30	558	2.4	8.6	2.8
		0	600	9.8	49.4	2.9
		-20	582	14.6	365.7	3.4
		-30	54	14.1	n.d.[(d)]	n.d.
	R = C_6H_5 **1-c**	30	280	2.9	17.1	3.2
		0	1010	6.4	55.5	3.4
		-20	641	8.2	230.8	2.9
		-30	76	7.9	n.d.	n.d.
	R= H **2-a**	30	1604	6.2	13.7	3.3
		0	1200	8.1	92.3	2.5
		-20	1170	8.9	43.0	3.9
	R = CH_3 **2-b**	30	239	6.5	30.5	2.8
		0	214	10.7	357.5	6.3
		-20	275	12.6	400.0	13.3
		-30	traces	n.d.	n.d	n.d.
	R = C_6H_5 **2-c**	30	215	6.1	26.1	2.9
		0	370	13.3	197.1	2.9
		-20	176	16.6	406.8	4.2
		-30	63	21.1	184.8	3.5
	R= H **3-a**	30	430	6.6	6.8	2.7
		0	800	11.6	114.9	2.3
		-20	567	11.7	143.8	5.9
	R = CH_3 **3-b**	30	1550	7.4	16.5	2.7
		0	590	11.3	461.7	2.7
		-20	288	11.6	710.9	5.2
		-30	traces	n.d.	n.d.	n.d.
	R = C_6H_5 **3-c**	30	770	7.6	16.3	2.5
		0	140	14.4	110.3	3.3
		-20	60	15.0	n.d.	n.d.
		-30	traces	n.d.	n.d.	n.d.
	w-4	30	61	8.1	n.d.	n.d.
		0	340	13.9	476.4	4.8
		-20	370	15.1	778.4	5.0
		-30	213	14.1	413.2	1.9

[(a)] Polymerisation conditions: toluene: 100 mL, [Zr] = 20x10^{-6} mol/L, [Al]/[Zr] = 3000, t = 30 min

[(b)] (kg PP)•(mol catalyst)$^{-1}$•h^{-1}

[(c)] Isotactic pentad contents by ^{13}C NMR; n.d. = not determined case we can observe a predominance of the isotactic heptad (indicated by an arrow in Figure 1) in the methyl region of ^{13}C NMR spectrum at 19.67 ppm from hexamethyldisiloxane (HMDS). The spectrum of the sample obtained with **3-c** (Figure 1L c) shows instead the pattern of an atactoid-like polypropylene, even if its atactic pentad content is practically the same as in the reference sample.

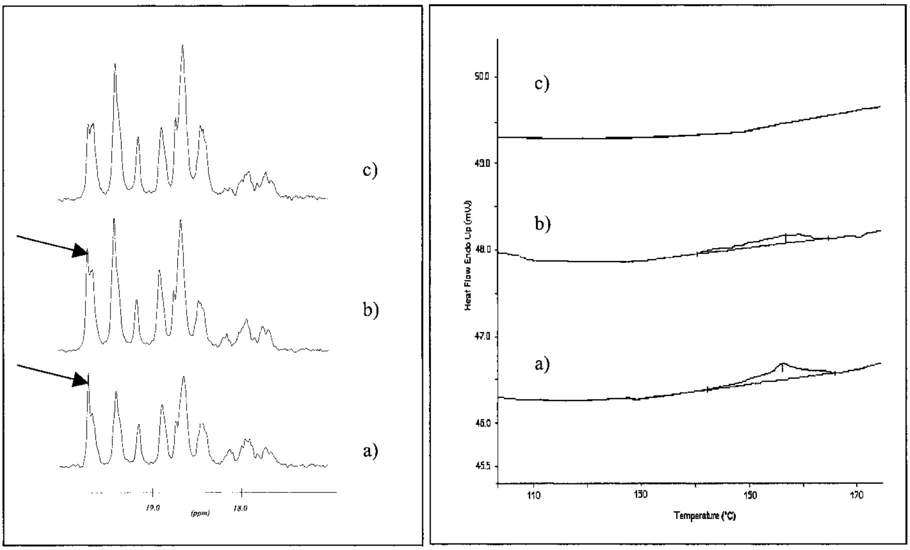


Figure 1. ^{13}C NMR spectra (Left) and the corresponding scanning calorimetry heating curves (Right) of polypropylene samples prepared with **w-4**, a), **2-c**, b) and **3-c**, c) at -20°C

This result was confirmed by the thermal analysis of the samples (Figure 1R) carried out by differential scanning calorimetry (DSC). In fact, the reference sample prepared with **w-4** (a) shows a detectable melting peak with a maximum at 156°C. The polypropylene prepared with **2-c** (b) also shows a slight melting peak, similar to that observed in the sample prepared with **w-4**, which allows us to hypothesise the formation of stereoblocks. As expected, the DSC curve of the sample prepared with **3-c** (c) is typical of a completely amorphous polypropylene, i.e. no melting peak was detected.

Titanium-Based Catalysts

Titanium-based complexes have been also investigated. For this study we made a selection among the zirconium-based catalysts, choosing the complex that gave the best results, i.e. the complex bearing the seven-membered ring associated with the phenyl substituent (**2-c Ti**). The titanium derivative (**w-4 Ti**) of the reference Waymouth catalyst was also synthesised and used under the same conditions.

In Table 2 the data obtained with the new titanium catalysts (**2-c Ti** and **w-4 Ti**) are reported and compared with those obtained with the corresponding zirconium complexes (**2-c** and **w-4**). Polymerisations have been carried out at the constant pressure of 2.4 atm at any given temperature (0 and -20 °C). Indeed, the simultaneous decrease of the temperature and increase of the pressure both raises the monomer concentration in solution (with the consequent enhancement of the propagation rate) and slows down the rate of interconversion of isospecific and aspecific states according to the proposed mechanistic model.[7] Both effects should be beneficial in increasing the length of the isotactic stereoblocks.

Table 2. Results of propylene polymerisation with Ti and Zr catalysts at 2.4 atm(a)

Catalyst	**T (° C)**	**Activity**b)	[*mmmm*]c) %	**N$_{iso}$**d)	**T$_m$ (°C)**
2-c	0	60	14.0	5.6	134
2-c	-20	47	17.4	5.9	131
2-cTi	0	141	5.5	5.6	142
2-cTi	-20	145	7.8	6.0	142
w-4	0	497	15.9	6.2	142
w-4	-20	149	17.6	6.3	145
w-4Ti	0	44	16.4	6.1	144

a)Polymerisation conditions: 100 mL toluene, P = 2.4 atm, [Mt] = $10x10^{-5}$ mol/L, [Al]/[Mt] = 1000, t = 60 min;
b)(kg PP)·(mol catalyst)$^{-1}$•h^{-1};
c)Isotactic pentad contents by ^{13}C NMR;
d)Average length of isotactic blocks estimated by ^{13}C NMR

The most interesting result is the high difference in stability between indenyl and tetrahydroindenyl titanium complexes compared with the corresponding zirconium analogues. In contrast to **w-4 Ti**, which is less stable with respect to **w-4**, and is consequently a less effective catalyst, **2-c Ti**, likely due to the saturated ring, is quite stable and more active with respect to the titanium reference catalyst **w-4 Ti**.

Other interesting results come from the study of the polymer microstructure by ^{13}C NMR (Figure 2L) and from the thermal behaviour by DSC (Figure 2R). Among the microstructural data the most striking result is that, although the isotactic pentad content is significantly lower with the titanium-based catalysts, the average length of the isotactic blocks (N_{iso}), estimated by ^{13}C NMR spectroscopy according to the formula $N_{iso} = 4 + 2\ ([mmmm]/[mmmr])$[8], is similar to that obtained with the zirconium based homologues. This result is confirmed by the analysis of the methyl region of the spectra of the samples prepared with **2-c Ti** (Figure 2L a) and **w-4 Ti**, where it is possible to appreciate the presence of a relatively intense signal of the [*mmmmmm*] heptad.

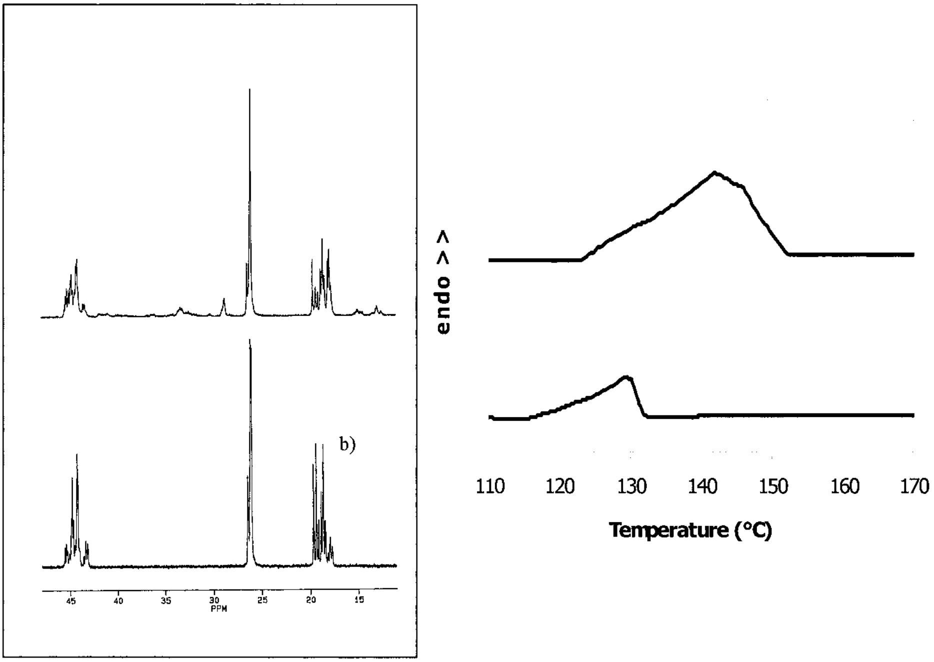


Figure 2. ^{13}C NMR spectra (Left) and the corresponding scanning calorimetry heating curves (Right) of polypropylene samples prepared with **2-c Ti**, a) and **2-c**, b) at -20 °C

Another significant difference observed in the spectrum of the titanium samples is the noticeable increase of the *rr* centred pentads, and the presence of a considerable amount of regioirregularities; these characteristics suggest a different polymerisation mechanism. Surprisingly, the DSC analysis shows a sensibly more evident melting peak in the sample from **2-c Ti.** The fractionation of this sample with boiling diethyl ether allowed the separation of two fractions of comparable amount. From the NMR spectra (Figure 3L) it is possible to conclude that the fractionation has successfully separated a fully atactic fraction (b) from a fraction (a) containing the 18% of isotactic pentad, in which the calculated average length of isotactic sequences reaches the value of 8.1.

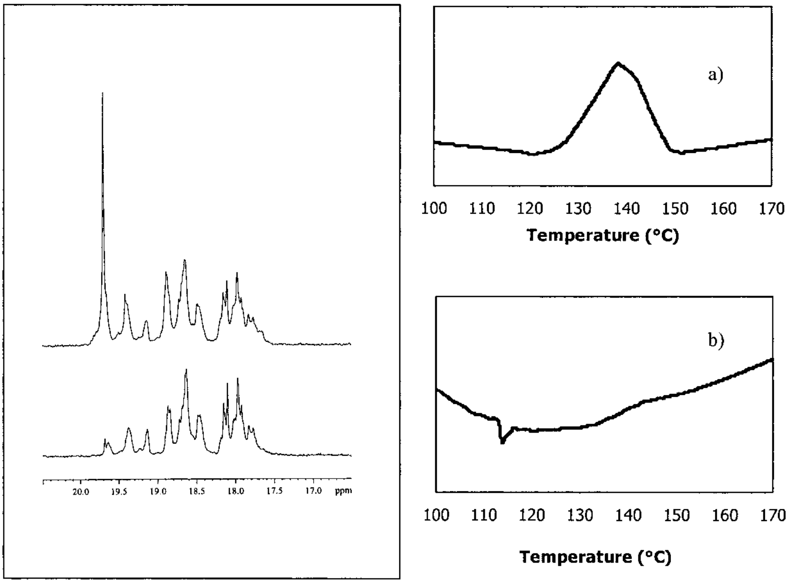


Figure 3. ^{13}C NMR spectra (Left) and DSC heating curves (Right) of ether insoluble fraction, a) and ether soluble fraction, b) of the polypropylene sample prepared with **2-c Ti** at -20 °C

Conclusions

Unbridged bicyclic metallocenes, where the ring fused to the cyclopentadienyl unit is saturated, constitute a very promising family of "fluxional" catalysts. The nature of the ligand has shown to have a marked effect on the stereoselectivity of these catalysts.[6] The present results show that the stereoselectivity is also quite sensitive to the nature of the metal atom (Ti *vs.* Zr). The titanium-based catalysts yield polypropylenes with new and interesting microstructures. In fact the decrease of the overall isotacticity is accompanied by a noticeable increase of the *rr* centred pentads. However, it is surprising that, despite the significantly lower isotactic pentad content [*mmmm*], the average lengths of the isotactic blocks (N_{iso}), calculated on the basis of the ^{13}C NMR analysis, are similar or even higher than those obtained with the zirconium based homologues. An ethyl ether insoluble fraction with a [*mmmm*] content of the 18% and a N_{iso} value of 8.1 can be separated, thereby demonstrating the stereoblock nature of the structures of these samples. Accordingly, the DSC analysis shows that the same samples are characterised by melting peaks which are equivalent to or more evident than those obtained by the zirconium homologues.

The present work also shows that titanium can also be used as a metal centre in "fluxional" catalysts if a saturated ring is fused to the cyclopentadienyl moiety, since this kind of ligand significantly increases the stability of its complexes. Up to now the easy decomposition of the indenyl titanium metallocenes had prevented their study and use in this field of catalysis.

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