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Synthesis and characterization of bis(indenyl) zirconium aryloxide derivatives and their use in α-olefin polymerization

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A series of new bis(indenyl) zirconium diaryloxides of general formula $Ind_2Zr(OL)_2$ ($L = C_6H_5$, 2; C_6F_5, 3; 2,6-$Me_2C_6H_3$, 4; 2,4,6-$Me_3C_6H_2$, 5; 4-$^tBuC_6H_4$, 6) were synthesized by a metathesis reaction of Ind_2ZrCl_2 (1) with the appropriate thallium aryloxide salt, TlOL. The complexes 1–6 were characterized by ^1H and ^{13}C NMR techniques. They were also examined as catalysts for ethene and 1-hexene polymerization with methylalumoxane as co-catalyst, and a trend of the polymerization activity as a function of aryloxide ligands was observed. An interpretation of this trend, considering both the electronic and steric effects of the substituents on the aryloxide rings, was proposed.

Keywords: zirconocene compounds; aryloxide; synthesis; polymerization; activity

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INTRODUCTION

Group 4 metallocenes find their main application in the field of olefin polymerization. Their use as polymerization catalysts in combination with an aluminium alkyl has been known for few decades,[1,2] but with the discovery of methylalumoxane (MAO)[3] in the 1970s, their study received a strong impulse. Much research has been dedicated to these compounds,[4–9] in particular to elucidate the correlation between ligand environment, catalytic activity and polymer microstructure. Information on the effects of σ-ligands other than methyl or chloride are, so far, quite limited, even if an increasing interest toward complexes bearing metal alkoxide bonds has been reported.[10–15] The chemistry of metal aryloxide derivatives and, in particular, of bis(cyclopentadienyl) zirconium diaryloxides, has been widely investigated. $(\eta^5\text{-}C_5Me_5)_2Zr(OPh)_2$ and $(\eta^5\text{-}C_5H_5)_2Zr(OPh)_2$ were synthesized by Howard *et al.*, who investigated the nature of the zirconium–oxo interaction by structural analyses.[13] Later, a series of bis(phenoxy) derivatives of Cp_2ZrCl_2 with different phenoxy steric-demanding groups was prepared by Repo *et al.* and used in ethene polymerization with MAO.[14]

We have also synthesized some new bis(indenyl) zirconium diaryloxide compounds, choosing the indenyl ligand to study the effect of this complexing group on the polymerization behaviour of these compounds when activated with MAO. To understand better the influence of the σ-ligands on the catalytic activity, we have chosen aryloxide derivatives bearing substituents with different steric and electronic properties.

EXPERIMENTAL

Materials and procedures

All operations and reactions were carried out in dry-boxes filled with purified nitrogen. Solvents were distilled under nitrogen from a potassium–benzophenone mixture (THF, toluene and *n*-hexane) or calcium hydride (dichloromethane). $ZrCl_4$ was purchased from Fluka and used as $ZrCl_4 \cdot 2$ THF.[16] All the thallium aryloxides (TlOL)

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Table 1 ^{1}H and ^{13}C NMR characterization (CD_2Cl_2) of complexes **1–6**

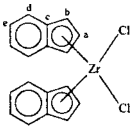
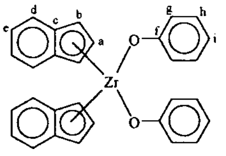
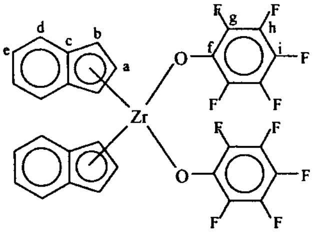
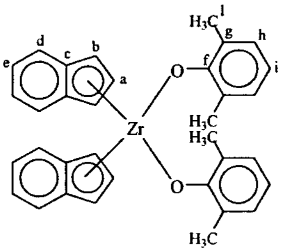
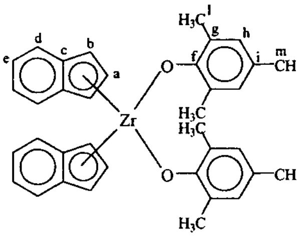
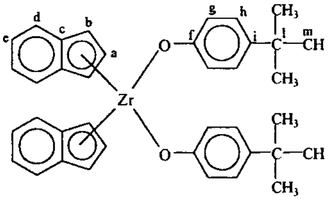
	^{1}H		^{13}C	
Compound	δ (ppm)[a]	H atom	δ (ppm)	C atom
Ind_2ZrCl_2 (**1**) 	7.59 (m; 4H)	e	127.00	c
	7.28 (m; 4H)	d	126.46	d
	6.49 (m; 2H)	a	125.40	e
	6.17 (d; 4H)	b	122.00	b
			104.18	a
$Ind_2Zr(OC_6H_5)_2$ (**2**) 	7.45 (m; 4H)	e	163.82	f
	7.14 (t; 4H)	h	134.28	c
	7.06 (m; 4H)	d	128.90	h
	6.77 (t; 2H)	i	124.73	d
	6.46 (d; 4H)	b	123.87	e
	6.44 (d; 4H)	g	120.50	g
	6.12 (m; 2H)	a	119.07	i
			118.63	b
			99.62	a
$Ind_2Zr(OC_6F_5)_2$ (**3**) 	7.34 (m; 4H)	e	161.93	f
	7.01 (m; 4H)	d	138.32	c
	6.34 (d; 4H)	b	128.46	h
	6.19 (m; 2H)	a	125.90	d
			123.28	e
			121.98	g
			120.98	i
			119.80	b
			99.97	a
$Ind_2Zr(O\text{-}2,6\text{-}Me_2C_6H_3)_2$ (**4**) 	7.40 (m; 4H)	e	161.59	f
	7.22 (t; 4H)	h	131.29	c
	7.14 (m; 4H)	d	128.96	h
	6.78 (d; 2H)	i	126.14	d
	6.43 (t; 4H)	b	124.48	e
	6.05 (m; 2H)	a	123.66	g
	2.17 (s; 12H)	l	120.82	i
			117.31	b
			101.05	a
			17.45	l
$Ind_2Zr(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2$ (**5**) 	7.36 (m; 4H)	e	161.84	f
	7.14 (m; 4H)	d	133.98	c
	6.69 (s; 4H)	h	128.69	h
	6.33 (d; 4H)	b	125.84	d
	6.02 (m; 2H)	a	124.52	e
	2.16 (s; 6H)	m	123.62	g
	2.16 (s; 12H)	l	121.48	i
			117.40	b
			100.78	a
			19.82	m
			16.95	l

Table 1 continued

	^{1}H		^{13}C	
Compound	δ (ppm)[a]	H atom	δ (ppm)	C atom
$Ind_2Zr(O\text{-}4\text{-}^{t}BuC_6H_4)_2$ (**6**) 	7.45 (m; 4H)	e	161.65	f
	7.16 (d; 4H)	h	141.77	i
	7.12 (m; 4H)	d	134.27	c
	6.40 (d; 4H)	b	125.54	h
	6.37 (d; 4H)	g	124.54	d
	6.09 (m; 2H)	a	123.88	e
	1.25 (s; 18H)	m	117.86	b
			117.20	g
			99.53	a
			34.00	l
			31.40	m

[a] The signal multiplicities and the integral values respectively are indicated in parentheses.

used were prepared from thallium ethoxide (Aldrich) and the parent phenol (Lancaster Synthesis) in toluene, where the TlOL salts were slightly soluble. The products were recovered by filtration as grey powders and analysed by elemental analysis, which corresponded to the TlOL formulation. MAO (Witco-Bergkamen, Germany, 10% w/w in toluene) was used without further purification. 1-Hexene (Aldrich) was distilled under nitrogen in the presence of calcium hydride and stored over molecular sieves. Polymerization-grade ethene was from SIAD (Bergamo, Italy).

The complexes were characterized by elemental analyses using a Fisons 1108 elemental analyser and by NMR spectroscopy using a Bruker AMX 300 spectrometer at ambient probe temperature, in CD_2Cl_2. Chemical shifts (as δ, in ppm) are reported versus tetramethylsilane and were determined using the residual proton solvent peak as the reference. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), multiplet (m) (see Table 1).

Syntheses

[Ind_2ZrCl_2] (1)

To a suspension of $ZrCl_4{\cdot}2THF$[16] (4 g, 10.6 mmol) in THF (70 ml) cooled to −78 °C, a solution of Li-indenyl[17] (2.6 g, 21.2 mmol) in THF was added dropwise. On gradual warming to ambient temperature a yellow solution formed. After 12 h of stirring, a yellow precipitate of **1** was obtained. The solution was filtered and the solid collected was washed and dried under reduced pressure (73% yield) and identified as bis(indenyl) zirconium dichloride by elemental analysis and by potentiometric titration for chloride determination.

Elem. Anal. Found: C, 54.1; H, 3.48; Cl, 18.01. Calc. for $C_{18}H_{14}ZrCl_2$: C, 54,96; H, 3.57; Cl, 18.07%.

[$Ind_2Zr(OC_6H_5)_2$] (2)

To a suspension of Ind_2ZrCl_2 (**1**) (200 mg, 0.5 mmol) in 15 ml of toluene, $TlOC_6H_5$ (304 mg, 1 mmol) was added. The reaction mixture was stirred for 18 h at room temperature, during which time TlCl was formed. After removing it by centrifugation, the solution was concentrated under reduced pressure and the pale-yellow solid obtained was recovered by precipitation with *n*-hexane, filtration and drying under vacuum (19% yield).

Elem. Anal. Found: C, 71.06; H, 4.81. Calc. for $C_{30}H_{24}O_2Zr$: C, 70.93; H, 4.73%.

[$Ind_2Zr(OC_6F_5)_2$] (3)

$Ind_2Zr(OC_6F_5)_2$ was prepared from **1** (200 mg, 0.5 mmol) and $TlOC_6F_5$ (396 mg, 1 mmol) as described above for the synthesis of **2**. Complex **3** was isolated as a pale-yellow product (37% yield).

Elem. Anal. Found: C, 52.29; H, 2.11. Calc. for $C_{30}H_{14}F_{10}O_2Zr$: C, 52.36; H, 2.04%.

[$Ind_2Zr(O\text{-}2,6\text{-}Me_2C_6H_3)_2$] (4)

Complex **4** was prepared from **1** (200 mg, 0.5 mmol) and $TlO\text{-}2,6\text{-}Me_2C_6H_3$ (349 mg, 1 mmol) as described for **2**, and was collected as a yellow solid (28% yield).

Elem. Anal. Found: C, 72.37; H, 5.71. Calc. for $C_{34}H_{32}O_2Zr$: C, 72.40; H, 5.68%.

[$Ind_2Zr(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2$] (5)
Complex **5** was prepared from **1** (200 mg, 0.5 mmol) and TlO-2,4,6-$Me_3C_6H_2$ (346 mg, 1 mmol) as described for **2**. The solvent was removed under reduced pressure to give a yellow solid (35% yield).

Elem. Anal. Found: C, 73.01; H, 6.07. Calc. for $C_{36}H_{36}O_2Zr$: C, 73.03; H, 6.08%.

[$Ind_2Zr(O\text{-}4\text{-}^tBuC_6H_4)_2$] (6)
Complex **6** was prepared from **1** (200 mg, 0.5 mmol) and TlO-4-$^tBuC_6H_4$ (361 mg, 1 mmol) as described for **2** and it was isolated as a pale-yellow product (20% yield).

Elem. Anal. Found: C, 73.57; H, 6.39. Calc. for $C_{38}H_{40}O_2Zr$: C, 73.60; H, 6.45%.

Polymerizations

Ethene polymerization

Polymerizations were carried out at 50 °C in a 1.5 l electrically heated autoclave equipped with a stirring bar. Reaction of **2** (run 2 in Table 2) is described as an example. Catalyst solution was prepared in a dry-box by dissolving 5 mg (9.8 μmol) of $Ind_2Zr(OC_6H_5)_2$ (**2**) in 20 ml of toluene in the presence of 1.4 ml (1.8 mmol) of MAO solution, and was transferred to a 100 ml stainless steel air-tight vessel. The autoclave was dried under nitrogen flux at 130 °C for 2 h and then cooled to room temperature. Afterwards, 300 ml of toluene, 6 ml (8 mmol) of MAO solution and 5 bar (30 g) of ethene were added. After heating the reaction mixture at 50 °C, the catalyst solution was injected. During the polymerization, the pressure was kept constant by feeding ethene, and the temperature was maintained within 50 ± 1 °C. When 10 g of ethene had been fed, the reaction was stopped by introducing 20 ml of isopropanol. The solid polymer was recovered by evaporation of the solvents, redissolution in toluene, reprecipitation with acidified methanol, filtration and drying *in vacuo*. The results obtained for the polymerization experiments are the average of two or more independent runs carried out for each complex.

1-Hexene polymerization

Polymerizations were performed in a dry-box at 23 °C using a 500 ml three-necked flask equipped with a magnetic stirring bar. Reaction of **2** (run 8 in Table 2) is described as an example. 200 ml of toluene, 6 ml (8 mmol) of MAO solution and 50 ml of 1-hexene were introduced into the flask. After 20 min, 5 mg (9.8 μmol) of $Ind_2Zr(OC_6H_5)_2$ (**2**) dissolved in 20 ml of toluene in the presence of 1.4 ml (1.8 mmol) of MAO solution was added to start the polymerization. The reaction was stirred for 3 h at room temperature, and then stopped by the addition of methanol. The polymer was isolated by evaporation of the solvents, then purified by redissolution in toluene, reprecipitation with acidified methanol, filtration and drying under reduced pressure.

Polyhexene characterization

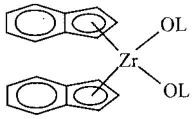
Identification of the polymers was performed by ^1H and ^{13}C NMR, dissolving the samples in $CDCl_3$. The olefinic protons of the end units of each polymer chain resonate at 4.67 ppm, and in the ^{13}C NMR the olefinic resonances were observed only at 110.20 and 147.90 ppm.[18]

RESULTS AND DISCUSSION

Bis(indenyl)complexes synthesis

Ind_2ZrCl_2 (**1**) was prepared by a modified literature procedure.[19] Indenyllithium[17] and THF-complexed zirconium tetrachloride ($ZrCl_4 \cdot 2THF$)[16] were reacted in a molar ratio of 2:1 at −78 °C in THF. This gave **1** as a yellow powder in high yield and good purity; its spectroscopic properties corresponded to those reported in the literature.[19] The main advantages to using the THF complex are to avoid the violent reaction that occurs when THF is added to anhydrous zirconium tetrachloride and to protect the metal complex from the disproportionation reaction that often occurs. The synthesis of $ZrCl_4 \cdot 2THF$ is conducted separately, using a simple method with high yield (91%) in dichloromethane at room temperature, as described in the literature.[16]

A series of bis(indenyl) zirconium diaryloxides of general formula $Ind_2Zr(OL)_2$ (Ind = indenyl; L = C_6H_5, **2**; C_6F_5, **3**; 2,6-$Me_2C_6H_3$, **4**; 2,4,6-$Me_3C_6H_2$, **5**; 4-$^tBuC_6H_4$, **6**, see Fig. 1) was prepared by a metathesis reaction of Ind_2ZrCl_2 (**1**) with two equivalents of the appropriate thallium salt, TIOL. We have used thallium derivatives as aryloxide transfer reagents for ease of separation of the TlCl by-product by centrifugation and for better control of the reaction stoichiometry. Complexes were recovered as yellow powders by precipitation with *n*-hexane, filtration, washing and drying (**2**–**4** and **6**), or by simple removal of the solvent under vacuum (**5**).



L	Compound
C_6H_5	2
C_6F_5	3
2,6-$Me_2C_6H_3$	4
2,4,6-$Me_3C_6H_2$	5
4-$^tBuC_6H_4$	6

Figure 1 The bis(indenyl) zirconium diaryloxides analysed.

Complexes **2**–**6** are rather sensitive to the oxygen and the moisture present in the atmosphere. For this reason, solutions for NMR analysis and solid samples for elemental analysis characterization were prepared under the nitrogen atmosphere of the dry-boxes. Attempts to grow crystals of these complexes from various solvents for X-ray diffraction studies were unsuccessful. However, the complete NMR characterization (^1H, ^{13}C and heteronuclear multiple quantum coherence (HMQC)) provided an unambiguous identification, as illustrated in Table 1.

^1H and ^{13}C NMR data of the complexes dissolved in CD_2Cl_2 are also collected in Table 1. The assignments were secured by HMQC experiments.

The ^1H NMR spectra of complexes **1**–**6** exhibit a typical AB_2 for the five-membered ring protons and an AA′BB′ pattern for the six-membered ring protons in the η^5-indenyl ligands.

The ^1H NMR signals of the unsubstituted aryloxide ligand exhibit a typical AA′BB′C pattern. The methyl or *t*-butyl groups as substituents in *meta, ortho*, and *para* positions of the aryl ring give a singlet, and cause a change in the chemical shifts and in the coupling of aryl protons.

Examining the data in Table 1, it seems that the proton H_a on the five-membered ring of the indenyls is the most sensitive to the nature of the σ-ligands. The highest difference in the H_a chemical shift can be detected on passing from the dichloride to the diaryloxide derivative, so that the order between δ H_a and δ H_b is inverted.

In all the complexes analysed, H_a exhibits a multiplet and the H_b protons are magnetically equivalent, as also revealed from the HMQC spectra, where only one signal is observed.

From the data in Table 1, it can be seen that the charge density on the indenyl ligands, and the relative ^1H and ^{13}C chemical shifts are very sensitive to the nature of the σ-ligands and of their substituents, as they have noticeable changes even without a specific trend. Only for the H_a nuclear proton does a regular shifting towards high fields occur, caused by an increase of the electron donor effect of the substituents on the aryloxide ligands.

Polymerization results

Metallocenes **2**–**6** were used as catalysts for ethene and 1-hexene polymerization, in the presence of

Table 2 α-Olefin polymerizations results

Run[a]	Catalyst	Monomer[b]	Time	Yield (g)	Activity (g pol/(g Zr h))
1	Ind_2ZrCl_2 (**1**)	E	2 min	16	414 × 10^3
2	$Ind_2Zr(OC_6H_5)_2$ (**2**)	E	3 min	9	201 × 10^3
3	$Ind_2Zr(OC_6F_5)_2$ (**3**)	E	4 min	13	297 × 10^3
4	$Ind_2Zr(O\text{-}2,6\text{-}Me_2C_6H_3)_2$ (**4**)	E	5 min	9	131 × 10^3
5	$Ind_2Zr(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2$ (**5**)	E	7 min	10	112 × 10^3
6	$Ind_2Zr(O\text{-}4\text{-}^tBuC_6H_4)_2$ (**6**)	E	6 min	12	164 × 10^3
7	Ind_2ZrCl_2 (**1**)	H	3 h	5	1439
8	$Ind_2Zr(OC_6H_5)_2$ (**2**)	H	3 h	0.5	186
9	$Ind_2Zr(OC_6F_5)_2$ (**3**)	H	3 h	1.5	761
10	$Ind_2Zr(O\text{-}2,6\text{-}Me_2C_6H_3)_2$ (**4**)	H	3 h	0.9	366
11	$Ind_2Zr(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2$ (**5**)	H	3 h	0.8	348
12	$Ind_2Zr(O\text{-}4\text{-}^tBuC_6H_4)_2$ (**6**)	H	3 h	1	416

[a] Ethene polymerization conditions: toluene = 320 ml, catalyst = 5 mg, cocatalyst = MAO, Al/Zr = 1000 (mol/mol), T = 50 °C, ethene pressure = 5 bar. 1-Hexene polymerization conditions: toluene = 220 ml, 1-hexene = 50 ml, catalyst = 5 mg, cocatalyst = MAO, Al/Zr = 1000 (mol/mol), T = 23 °C.

[b] E = ethene, H = 1-hexene.

poly-MAO as cocatalyst. Tests were also performed with **1** for comparison.

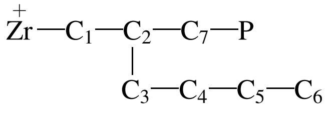
The results reported in Table 2 show that the dichloride derivative **1** is the most active catalyst, both in ethene and 1-hexene polymerization, as already observed with regard to other indenyl catalysts.[4] When the aryloxide ligands are fluorinated (**3**), the polymerization activity increases considerably with respect to the corresponding unsubstituted complex (**2**). Alkyl-substituted aryloxide compounds **4**, **5** and **6** were found to be less efficient catalysts, and similar polymerization activities were observed among them. The productivity depends on the type of aryloxide, and decreases in the order:

$$OC_6F_5 > OC_6H_5 > O\text{-}4\text{-}{}^tBuC_6H_4 > O\text{-}2,6\text{-}Me_2C_6H_3 > O\text{-}2,4,6\text{-}Me_3C_6H_2$$

A similar trend was followed also by metallocenes-type $Cp_2Zr(OL)_2$, as reported in our previous paper,[15] even though $Cp_2Zr(OAr)_2$ ($OAr = 2,6\text{-}OC_6H_3Me_2$; $2,4,6\text{-}OC_6H_2Me_3$; $4\text{-}OC_6H_4\,{}^tBu$) present a significantly higher activity at 90 °C than the parent compound Cp_2ZrCl_2, which in turn shows a higher activity than the corresponding dichloride indenyl compound. The lower reactivity of indenyl zirconium derivatives compared with those of the equivalent series of cyclopentadienyl zirconium compounds is probably due to the higher steric hindrance given by the indenyl ligand.

Polyhexene characterization

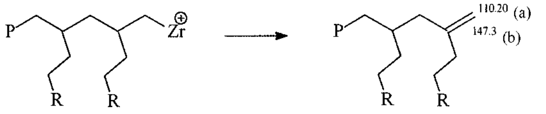
Polymerization of 1-hexene with **1**–**6**, with MAO as cocatalyst, affords an oily polyhexene, probably having low molecular weight. Its tacticity was deduced from clean ^{13}C NMR resonances, whose values are very similar for all the polymers obtained by using all the catalysts analysed. Figure 2 shows, as an example, the typical spectrum of polyhexene obtained by using **5** as catalyst; the characteristic peaks are localized at 40.26 (C_1), 34.74 (C_3), 32.27 (C_2), 28.68 (C_4), 23.24 (C_5), and 14.18 ppm (C_6) according to the following arrangement:



$$\overset{+}{Zr}—C_1—\underset{\textstyle C_3—C_4—C_5—C_6}{\underset{|}{C_2}}—C_7—P$$

By comparing our ^{13}C NMR resonances with those reported in the literature[18,20–22] it can be determined whether the polymers are isotactic or syndiotactic; in our case, the chemical shifts always correspond to those typical of isotactic polyhexene.

End-group analysis by ^1H NMR spectroscopy in the olefinic regions reveals much about the mechanism of chain termination. Multiplet resonances at 4.67 ppm may be attributed to the vinylidene end group of the polymeric chain dissociated via β-hydrogen elimination from the Zr—$C_{polymer}$ bond; consequently, it can be inferred that polymeric chain formation occurs through 1,2 insertion of the 1-hexene monomer.[21] The ^{13}C NMR chemical shifts gives information about the pathway of formation of the end group (Scheme 1; P = growing polymeric chain).[23]



Scheme 1

Polymerization discussion

In a metallocene, the substituents on the ligands bring about both electronic and steric effects. Taking into account these effects, we can satisfactorily interpret the productivity trend observed above. The highest polymerization activity of the dichloride derivative **1** with respect to the aryloxide activities could be explained by considering that the Zr—O bond strength (776.1 kJ mol^{-1}) is stronger than that of Zr—Cl (489.5 kJ mol^{-1}), and thus is more difficult to be cleaved.[24] We can also hypothesize a role for the steric hindrance of the aryloxide ligand, which prevents the formation of the catalytically active species.

When the aryloxide ligand is fluorinated (**3**), electron withdrawal enhances polarization of the Zr—O bond and increases the activation of the catalyst. The introduction of electron-donating alkyl radicals (i.e. methyl or *t*-butyl groups) produces an inductive effect on the ring. This affects the nature of the Zr—O bond, which becomes less polarized, and then the complex becomes less inclined to activation. We have also not excluded that a role is played by the steric effect of these substituents. By comparison of polymerization results of runs 4 and 10 with runs 6 and 12 respectively (see Table 2), we can hypothesize that the presence of two methyl groups in positions 2 and 6 (complexes **4** and **5**) does not favour the activation of the catalyst with respect to the

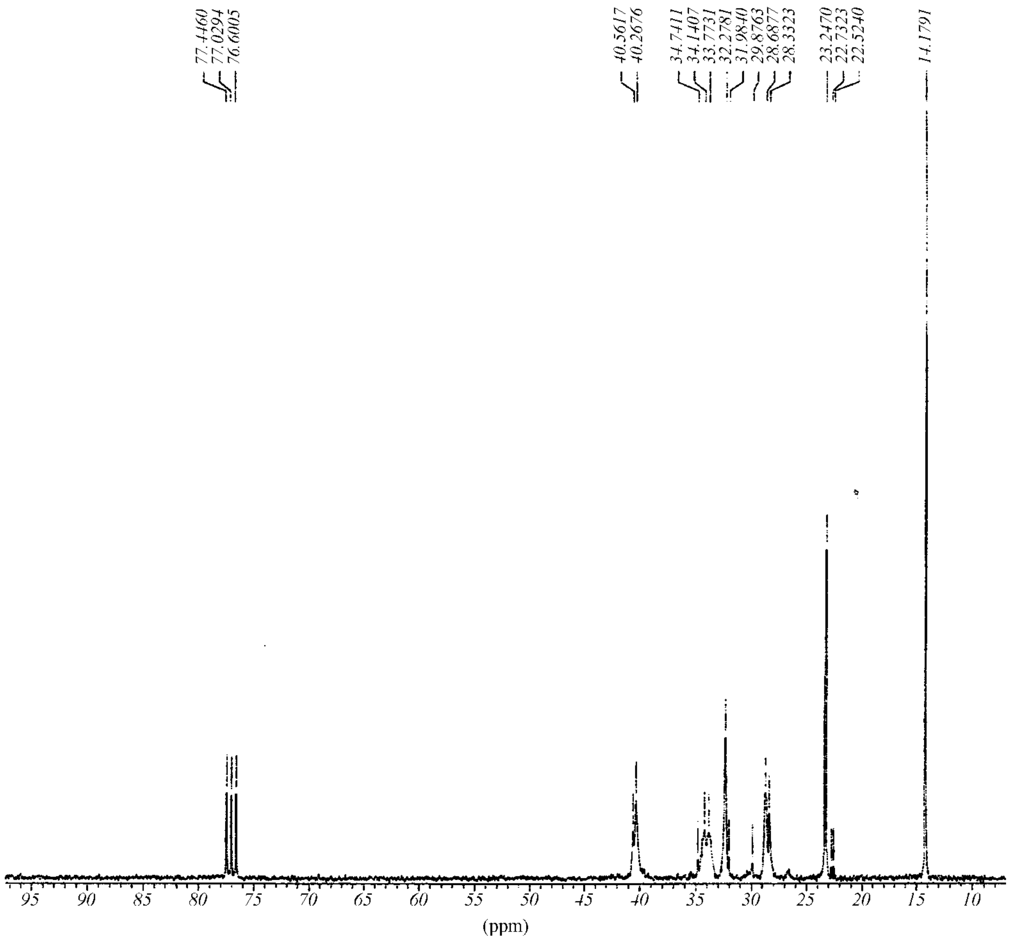


Figure 2 NMR polyhexene spectrum obtained by using [$Ind_2Zr(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2$] (**5**) as catalyst.

presence of a bulkier *t*-butyl group (complex **6**) in position 4.

The results reported above show the polymerization behaviour of the new zirconium aryloxide derivatives, and underscore the role played by both electronic and steric effects on the σ-ligands of a metallocene.

CONCLUSIONS

New bis(indenyl) zirconium diaryloxides were synthesized and characterized. The complexes were used as catalysts in ethene and 1-hexene polymerization with MAO, and an interesting trend of polymerization activity as a function of the aryloxide ligands was observed. An interpretation of this trend considering both the electronic and steric effects of the substituents on the aryloxide rings was attempted.

Polyhexene characterization reveals that samples obtained from the different bis(indenyl) zirconium diaryloxides are very similar in terms of molecular weight, isotacticity index and chain end-group. This leads us to hypothesize that the polymerization mechanism is the same for all the compounds, and that only one catalytically active species is formed with MAO, probably produced by the substitution of one or both aryloxides with one or two methyl groups and by their subsequent coordination to the aluminium metal. Nevertheless, the reason for which the R_2ZrX_2 compounds have a reactivity that depends on the nature of the X group is still not well understood.

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