Metallocene analogues containing bulky heteroallylic ligands and their use as new olefin polymerization catalysts

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Abstract

A series of Ti and Zr metallocene analogues containing bulky benzamidinate ligands has been prepared and fully characterized. Treatment of $TiCl_4(THF)_2$ or $ZrCl_4(THF)_2$ with two equivalents of the appropriate benzamidinate anions affords the bis(benzamidinato) complexes $[C_6H_5C(NC_3H_7)_2]_2MCl_2$ (M = Ti (**1**), Zr (**2**)) and $[C_6H_5C(NC_6H_{11})_2]_2MCl_2$ (M = Ti (**3**), Zr (**4**)). The zirconium complex **2** was structurally characterized by X-ray diffraction. In a similar manner the nonafluoromesityl derivative $[(CF_3)_3C_6H_2C(NC_6H_{11})_2]_2ZrCl_2$ (**5**) was synthesized from $ZrCl_4(THF)_2$ and $Li[(CF_3)_3C_6H_2C(NC_6H_{11})_2]$. Methylation of **4** with methyllithium yields the dimethyl complex $[C_6H_5C(NC_6H_{11})_2]_2ZrMe_2$ (**6**). The mixed-ligand metallocene analogues $[C_6H_5C(NC_3H_7)_2](C_5Me_5)MCl_2$ (M = Ti (**7**), Zr (**8**)) and $[C_6H_5C(NC_6H_{11})_2](C_5Me_5)TiCl_2$ (**9**) have been prepared by reacting $(C_5Me_5)TiCl_3$ or $(C_5Me_5)ZrCl_3$ with one equivalent of a lithium N,N''-dialkylbenzamidinate. The polymerization of ethylene and propylene has been studied by the catalytic precatalyst complexes **1** and **2** upon reaction of an excess of methylalumoxane to obtain the active cationic complexes. The polymerization activity of the complexes is comparable to other benzamidinate ancillary containing ligands although toward shorter amounts of time due to a competitive inhibition presumably obtained by a β-hydrogen elimination from the ligand. Polymerization activity is strongly dependent on catalyst and cocatalyst concentrations and on temperature. © 1998 Elsevier Science B.V.

Keywords: Heteroallylic ligands; Metallocene analogues; Zirconium complexes; Olefin polymerization

1. Introduction

Following our discovery that analogues of metallocene catalysts can be obtained with the use of bulky heteroallylic ligands [1–3], this class of compounds has attracted considerable interest. Especially the synthesis of bis(benzamidinato) metal dihalides of Ti, Zr, and Hf appears to be a promising approach to new classes of olefin polymerization catalysts [4–10].

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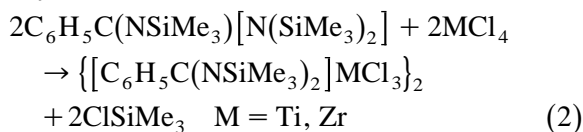Such complexes usually contain the benzamidinate ligands in a chelating coordination mode:
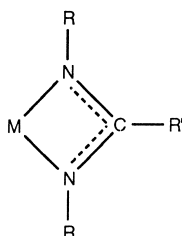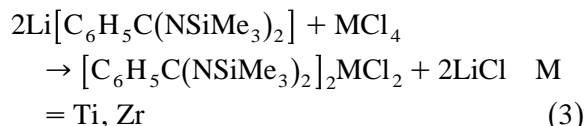

In most cases the substituents R and R′ are alkyl, aryl or $SiMe_3$, but examples with R and R′ = H or NMe_2 are also known. Typical synthetic routes to such benzamidinato complexes involve reactions of transition metal halides with alkali metal benzamidinates [11–16] or the parent amidines [17]. In some cases carbodiimides have been employed as precursors in insertion reactions. For example, bis(cyclopentadienyl)diphenylzirconium(IV) reacts with *p*-toluyl-carbodiimide under formation of an N-aryl substituted zirconium benzamidinate complex (Eq. (1)) [18]:

$$(C_5H_5)_2Zr(C_6H_5)_2 + RN=C=NR \longrightarrow$$

$$R = \underset{}{\bigcirc} - Me$$

$$(1)$$
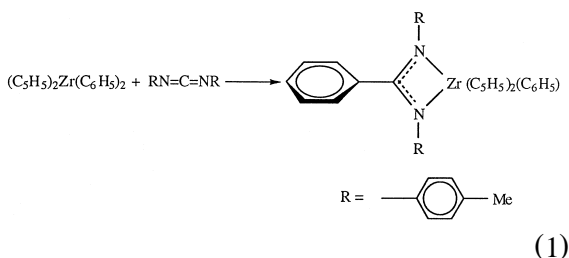
In the case of titanium and zirconium, benzamidinate complexes containing *N*-trimethylsilyl substituents form the most thoroughly investigated class of compounds. The first examples were reported by Dehnicke et al. in 1988 [19]. They were prepared according to Eq. (2) by treatment of the metal tetrachlorides with equimolar amounts of *N,N,N′*-tris(trimethylsilyl)benzamidine:

$$2C_6H_5C(NSiMe_3)\left[N(SiMe_3)_2\right] + 2MCl_4$$
$$\rightarrow \left\{\left[C_6H_5C(NSiMe_3)_2\right]MCl_3\right\}_2$$
$$+ 2ClSiMe_3 \quad M = Ti, Zr \qquad (2)$$

In the solid state, both compounds form dimers in which the metal atoms are connected via chlorine bridges. In the same year Roesky et al. described the preparation of disubstituted complexes by simple treatment of the metal tetrachlorides with lithium-*N,N′*-bis(trimethylsilyl)benzamidinate in a 1:2 molar ratio (Eq. (3)) [20]:
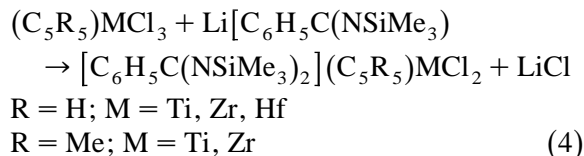
$$2Li\left[C_6H_5C(NSiMe_3)_2\right] + MCl_4$$
$$\rightarrow \left[C_6H_5C(NSiMe_3)_2\right]_2MCl_2 + 2LiCl \quad M$$
$$= Ti, Zr \qquad (3)$$

The X-ray diffraction studies of $[C_6H_5C(NSiMe_3)_2]_2TiCl_2$ obtained by Roesky et al. [20] and the analogous $[C_6H_5C(NSiMe_3)_2]_2ZrCl_2$ obtained by Eisen et al. [5] revealed in both cases the presence of monomeric molecules, in which the central metal is octahedrally coordinated by the two chelating benz-

amidinate ligands and two chlorine atoms. The chlorine atoms in the metallocene dichloride analogues can be replaced stepwise by σ-alkyl ligands. For example, the methyl derivatives $[C_6H_5C(NSiMe_3)_2]_2M(Me)Cl$ and $[C_6H_5C(NSiMe_3)_2]_2MMe_2$ (M = Ti, Zr) have been synthesized by methylation of the chloro precursors using either methyllithium or dimethylmagnesium [7,21]. Independently, $[C_6H_5C(NSiMe_3)_2]_2TiMe_2$ has been obtained in a protolytic reaction by treatment of tetramethyltitanium with *N,N′*-bis(trimethylsilyl)benzamidine. The dimethyltitanium complex has been structurally characterized by X-ray diffraction [21].

Several *N*-silylated mono(cylopentadienyl) benzamidinato complexes of group IV elements have also been reported. Edelmann et al. prepared the first mixed-ligand complex of this type, $[C_6H_5C(NSiMe_3)_2](C_5H_5)TiCl_2$, by reacting $(C_5H_5)TiCl_3$ with the corresponding sodium benzamidinate [22], while Roesky et al. prepared the difluoro complex $[MeOC_6H_4C(NSiMe_3)_2](C_5Me_5)TiF_2$ from $(C_5Me_5)TiF_3$ and $Li[MeOC_6H_4C(NSiMe_3)_2]$ [23]. More recently, Green et al. described a

straightforward synthetic route to metallocene analogues of the type $[C_6H_5C(NSiMe_3)_2]$ $(C_5R_5)MCl_2$ [6]:

$$(C_5R_5)MCl_3 + Li[C_6H_5C(NSiMe_3)$$
$$\rightarrow [C_6H_5C(NSiMe_3)_2](C_5R_5)MCl_2 + LiCl$$

R = H; M = Ti, Zr, Hf

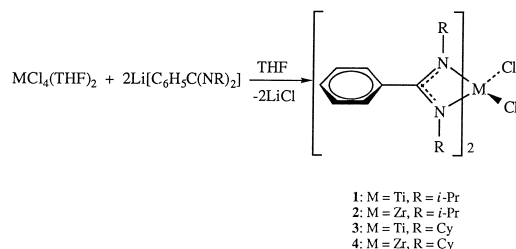R = Me; M = Ti, Zr   (4)

Meanwhile several research groups have demonstrated the utility of metallocene analogues containing bulky heteroallylic ligands as novel homogeneous catalysts. Catalyst systems comprising bis(benzamidinato) zirconium dichlorides have been found to catalyze the polymerization of ethylene, propylene and styrene, although the catalytic activities are generally significantly lower than those of comparable metallocene derivatives [4–10]. A considerable disadvantage is the pronounced moisture-sensitivity of complexes containing *N*-trimethylsilyl substituted benzamidinate ligands. This is due to the inherent hydrolytic instability imposed by the presence of several Si–N bonds in the molecules. A suitable approach to hydrolytically more robust catalysts appeared to be the use of *N-alkylated* benzamidinate anions as ancillary ligands. In this paper we report the synthesis of several titanium and zirconium bis(benzamidinate) as well as mixed-ligand catalysts which display a greatly improved hydrolytic stability due to the use of N,N^1-dialkylbenzamidinate anions as supporting ligands. In addition, catalytic activity studies toward the polymerization of ethylene and propylene promoted by complexes **1** and **2** are presented.

2. Results and discussion

2.1. Preparation of bis(benzamidinato) metal dichlorides, $[C_6H_5C(NC_3H_7)_2]_2MCl_2$ (M = Ti (**1**), Zr (**2**)) and $[C_6H_5C(NC_6H_{11})_2]_2MCl_2$ (M = Ti (**3**), Zr (**4**))

Reactions of $TiCl_4(THF)_2$ and $ZrCl_4(THF)_2$ with two equivalents of $Li[C_6H_5C(NC_3H_7)_2]$

or $Li[C_6H_5C(NC_6H_{11})_2]$, respectively, afforded the disubstituted complexes **1–4** as wine-red (M = Ti) or yellow (M = Zr) crystalline solids (Eq. (5)):

$$MCl_4(THF)_2 + 2Li[C_6H_5C(NR)_2] \xrightarrow[-2LiCl]{THF}$$

1: M = Ti, R = *i*-Pr
2: M = Zr, R = *i*-Pr
3: M = Ti, R = Cy
4: M = Zr, R = Cy

(5)

All four products are stable in air for several days and they are thus significantly less sensitive to hydrolysis than the corresponding *N*-trimethylsilyl derivatives. Full characterization by elemental analysis as well as IR and NMR (^{1}H, ^{13}C) spectroscopy is simple and straightforward. EI mass spectra of the titanium complexes **1** and **3** show the molecular ions (**1**: m/z 524, **3**: m/z: 686), whereas in the spectra of the zirconium derivatives only fragment peaks due to the benzamidinate ligands are observed. The most prominent characteristic bands in the IR spectra result from absorptions of the NCN chelate unit. These bands appear at 1635 and 1639 cm^{-1} as antisymmetrical and at 1346 and 1349 cm^{-1} as symmetrical NCN valence vibration.

2.2. Crystal structure determination of $[C_6H_5C(NC_3H_7)_2]_2ZrCl_2$ (**2**)

The crystallographic data for complex **2** are given in Tables 1, 3 and 4. Suitable single crystals of **2** were obtained by the slow cooling of a saturated solution in toluene from 20°C to −25°C. Fig. 1 shows the structure of the monomeric molecule. The central Zr atom is octahedrally surrounded by two chelating benzamidinate ligands and two terminal chlorine atoms. One chlorine atom (Cl (1a)) and one nitrogen atom of a chelate unit (N (2a)) are in

the axial positions, while the second Cl atom and the remaining nitrogen atoms occupy the equatorial positions. As a result the C–N bond lengths of the two chelate units are slightly different (132 and 135 pm). The identical Zr–N distances (221 and 222 pm) are somewhat longer than in the dimeric zirconium benzamidinate $[C_6H_5C(NSiMe_3)_2ZrCl_3]_2$ (214 and 219 pm) [19] though alike in the monomeric $[C_6H_5C(NSiMe_3)_2]_2ZrCl_2$ (220 and 224) [5].

Especially remarkable is the large torsion angle between the two planar $ZrCN_2$ rings, which are almost perpendicular with respect to each other (89.2°). This situation obviously minimizes repulsion between the bulky isopropyl groups in the molecule, as illustrated in Fig. 2. The torsion angles between the phenyl rings and the $ZrCN_2$ planes are 89.3°, which is the highest value found for any metal benzamidinate complex. In $[C_6H_5C(NSiMe_3)_2]_2SbCl_2$ this torsion

Table 1
Bond lengths (pm) and angles (°) for complex **2**

Zr(1)–N(1)	220.8(4)	Zr(1)–N(1)#1	220.8(4)
Zr(1)–N(2)#1	222.0(4)	Zr(1)–N(2)	222.0(4)
Zr(1)–Cl(1)#1	240.99(14)	Zr(1)–Cl(1)	240.99(14)
Zr(1)–C(1)#1	264.8(4)	Zr(1)–C(1)	264.8(4)
N(1)–C(1)	134.6(6)	N(1)–C(11)	147.2(6)
N(2)–C(1)	131.5(6)	N(2)–C(21)	146.2(7)
C(1)–C(2)	149.5(7)	C(2)–C(7)	138.4(7)
C(2)–C(3)	139.1(7)	C(3)–C(4)	138.1(7)
C(4)–C(S)	137.3(8)	C(5)–C(6)	137.0(8)
C(6)–C(7)	139.1(7)	C(11)–C(13)	150.9(8)
C(11)–C(12)	151.3(8)	C(21)–C(22)	150.3(10)
C(21)–C(23)	153.6(11)		
N(1)–Zr(1)–N(1)#1	153.5(2)	N(1)–Zr(1)–N(2)#1	100.0(2)
N(1)#1–Zr(1)–N(2)#1	60.05(14)	N(1)–Zr < 1)–N(2)	60.05(14)
N(1)#1–Zr(1)–N(2)	100.0(2)	N(2)#1–Zr(1)–N(2)	89.2(3)
N(1)–Zr(1)–Cl(1)#1	104.35(11)	N(1)#1–Zr(1)–Cl(1)#1	93.16(10)
N(2)#1–Zr(1)–Cl(1)#1	153.04(12)	N(2)–Zr(1)–Cl(1)#1	92.90(14)
N(1)–Zr(1)–Cl(1)	93.16(10)	N(1)#1–Zr(1)–Cl(1)	104.35(11)
N(2)#1–Zr(1)–Cl(1)	92.90(14)	N(2)–Zr(1)–Cl(1)	153.04(12)
Cl(1)#1–Zr(1)–Cl(1)	97.14(9)	N(1)–Zr(1)–C(1)#1	128.6(2)
N(1)#1–Zr(1)–C(1)#1	30.49(14)	N(2)#1–Zr(1)–C(1)#1	29.7(2)
N(2)–Zr(1)–C(1)#1	97.4(2)	Cl(1)#1–Zr(1)–C(1)#1	123.64(11)
Cl(1)–Zr(1)–C(1)#1	97.65(11)	N(1)–Zr(1)–C(1)	30.49(14)
N(1)#1–Zr(1)–C(1)	128.6(2)	N(2)#1–Zr(1)–C(1)	97.4(2)
N(2)–Zr(1)–C(1)	29.7(2)	Cl(1)#1–Zr(1)–C(1)	97.65(11)
Cl(1)–Zr(1)–C(1)	123.64(11)	C(1)#1–Zr(1)–C(1)	117.4(2)
C(1)–N(1)–C(11)	122.7(4)	C(1)–N(1)–Zr(1)	93.2(3)
C(11)–N(1)–Zr(1)	141.5(3)	C(1)–N(2)–C(21)	123.5(5)
C(1)–N(2)–Zr(1)	93.5(3)	C(21)–N(2)–Zr(1)	142.5(4)
N(2)–C(1)–N(1)	112.7(4)	N(2)–C(1)–C(2)	124.4(4)
N(1)–C(1)–C(2)	122.9(4)	N(2)–C(1)–Zr(1)	56.8(2)
N(1)–C(1)–Zr(1)	56.4(2)	C(2)–C(1)–Zr(1)	174.3(3)
C(7)–C(2)–C(3)	119.0(5)	C(7)–C(2)–C(1)	120.2(4)
C(3)–C(2)–C(1)	120.7(4)	C(4)–C(3)–C(2)	119.8(4)
C(5)–C(4)–C(3)	120.9(5)	C(6)–C(5)–C(4)	119.7(5)
C(5)–C(6)–C(7)	120.1(5)	C(2)–C(7)–C(6)	120.4(5)
N(1)–C(11)–C(13)	110.7(5)	N(1)–C(11)–C(12)	110.0(4)
C(13)–C(11)–C(12)	111.9(5)	N(2)–C(21)–C(22)	110.8(6)
N(2)–C(21)–C(23)	108.6(6)	C(22)–C(21)–C(23)	110.5(5)

Symmetric transformation for the equivalent atoms: #1 $-x,\ y,\ -z+1/2$.

Table 2

Activity data for the polymerization of ethylene and propylene by bis(benzamidinate) zirconium and titanium complexes

Entry	Catalyst[a]	T (°C)	[Cat][b]	[Co-cat][c]	Al:M ratio	α-olefin	Activity[d]	mp (°C)
1	**1**	25	4.4×10^{-4}	0.088	200	ethylene	1.2×10^5	129.8
2	**2**	0	4.4×10^{-4}	0.352	800	ethylene	1.4×10^4	135.7
3	**2**	25	4.4×10^{-4}	0.088	200	ethylene	6.8×10^3	136.6
4	**2**	25	4.4×10^{-4}	0.176	400	ethylene	3.4×10^4	133.3
5	**2**	25	4.4×10^{-4}	0.352	800	ethylene	5.6×10^4	133.4
6	**2**	25	4.4×10^{-4}	0.880	2000	ethylene	6.0×10^4	134.4
7	**2**	60	4.4×10^{-4}	0.176	400	ethylene	8.6×10^4	130.9
8	**2**	60	4.4×10^{-4}	0.352	800	ethylene	2.1×10^5	131.8
9	**2**	60	4.4×10^{-4}	0.440	1000	ethylene	1.8×10^5	131.7
10	**2**	60	4.4×10^{-4}	0.880	2000	ethylene	4.0×10^5	133.0
11	**1**	25	4.4×10^{-4}	0.176	400	propylene	9.5×10^3	
12	**2**	25	4.4×10^{-4}	0.176	400	propylene	6.8×10^3	
13	**2**	25	4.4×10^{-4}	0.440	1000	propylene	1.4×10^4	
14	**2**	25	4.4×10^{-4}	1.760	4000	propylene	2.1×10^4	
15	**2**	60	4.4×10^{-4}	0.440	1000	propylene	2.1×10^4	
16	**2**	60	4.4×10^{-4}	0.880	2000	propylene	1.4×10^4	

[a] Polymerization time = 5 min.

[b] [Catalyst], M in toluene.

[c] [Co-catalyst], M in toluene, methylaluminoxane, solvent removed from a 20% solution in toluene (Schering) at $25°C / 10^{-6}$ Trr [monomer], pressure = 1 atm.

[d] Grams total polymer/mol Zr atm ethylene h.

Table 3

Crystal data, data collection and refinement for **2**

Empirical formula	$C_{26}H_{38}Cl_2N_4Zr$
Formula weight	568.72
Temperature	223(2) K
Wavelength	71.073 pm
Crystal system	orthorhombic
Space group	Pbcn
Unit cell dimensions	$a = 2047.7(5)$ pm
	$b = 851.110(10)$ pm
	$c = 1685.3(4)$ pm
Volume	$2.9371(11)$ nm^3
Z	4
Density (calculated)	1.286 mg/m^3
Absorption coefficient	0.576 mm^{-1}
F(000)	1184
Crystal size	$0.90 \times 0.70 \times 0.20$
θ-range for data collection	3.54 to 22.48°
Index ranges	$-22 \leq h \leq 22, -1 \leq k \leq 9, -18 \leq l \leq 18$
Reflections collected	2248
Independent reflections	1902 ($R_{int} = 0.0544$)
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	1898/0/154
Goodness-of-fit on F^2	1.118
Final R indices:	
$R_1 [I > 2\sigma(I)]$	0.0581
wR_2	0.1489
R indices (all data):	
R_1	0.0652
wR_2	0.1644
Largest difference peak	1196 e nm^{-3}
Largest difference hole	-757 e nm^{-3}

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for complex **2**

	X	Y	Z	U(eq)
Zr(1)	0	517(1)	2500(1)	40(1)
Cl(1)	375(1)	−1356(2)	3471(1)	79(1)
N(1)	1001(2)	1111(4)	2115(2)	45(1)
N(2)	157(2)	2374(5)	1595(3)	60(1)
C(1)	791(2)	2133(5)	1562(3)	46(1)
C(2)	1239(2)	2906(5)	980(3)	45(1)
C(3)	1372(3)	2208(6)	251(3)	57(1)
C(4)	1793(3)	2933(6)	−274(3)	61(1)
C(5)	2084(1)	4339(6)	−88(3)	57(1)
C(6)	1945(3)	5053(7)	621(3)	59(1)
C(7)	1525(2)	4336(6)	1159(3)	55(1)
C(11)	1674(2)	504(6)	2133(3)	54(1)
C(12)	1682(3)	−1207(7)	1889(4)	81(2)
C(13)	1976(3)	749(8)	2940(4)	76(2)
C(21)	−191(3)	3442(8)	1063(4)	86(2)
C(22)	−552(4)	2539(11)	434(4)	109(3)
C(23)	−667(4)	4437(7)	1557(5)	103(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

angle is 88.9° [24]. With 112.7° the N(1)–C(1)–N(2) is slightly smaller than the comparable angle in $[C_6H_5C(NSiMe_3)_2ZrCl_3]_2$ (114.9°) [19] or in $C_6H_5C(NSiMe_3)_2ZrCl_2$ (114.7°) [5].

2.3. Preparation of $[(CF_3)_3C_6H_2C(NC_6H_{11})_2]_2ZrCl_2$ (**5**)

Similar treatment of $ZrCl_4(THF)_2$ with the nonafluoromesityl substituted lithium-N,N'-dicyclohexylbenzamidinate $Li[(CF_3)_3C_6H_2C(NC_6H_{11})_2]$ (molar ratio 1:2) afforded the dis-
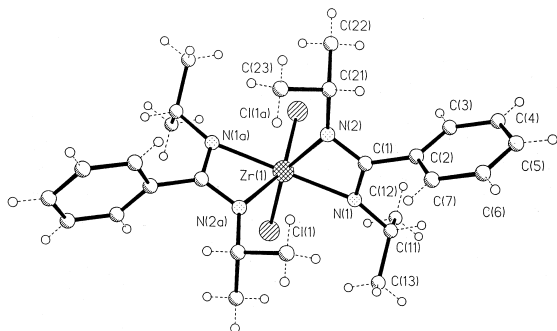

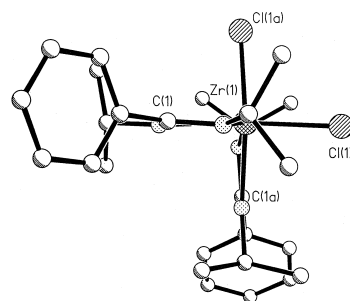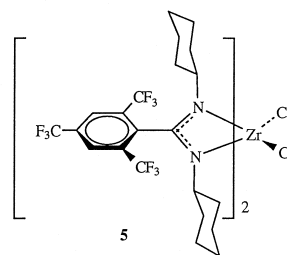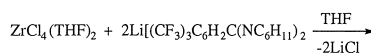Fig. 1. The molecular structure of **2** showing the atom numbering scheme.

Fig. 2. Side view of the molecular structure of complex **2**.

ubstitution product **5** in low yield (24%) as a cream-colored solid which decomposes at 161°C (Eq. (6)).

$$ZrCl_4(THF)_2 + 2Li[(CF_3)_3C_6H_2C(NC_6H_{11})_2] \xrightarrow[-2LiCl]{THF}$$


(6)

The low yield is due to the formation of large amounts of oily by-products. Purification of the crude material can only be achieved by recrystallization from hexane, which results in considerable losses due to the high solubility of **5**.

2.4. Preparation of $[C_6H_5C(NC_6H_{11})_2]_2ZrMe_2$ (**6**)

The chlorine atoms in **4** are readily replaced by methyl groups upon treatment with two equivalents of methyllithium (Eq. (7)). The reaction proceeds smoothly in diethylether and affords the dimethyl derivative **6**. The product melts at 135°C without decomposition, indicating a higher thermal stability than the dichloride precursor. A similar observation has earlier been

reported for the dimethylzirconium complex (^{t}Bu$_3$CO)$_2$ZrMe$_2$ [25].

(7)
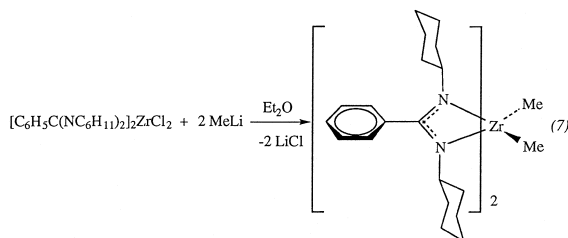
Dichloro or dialkyl complexes [6]such as **1**–**6** are useful precursors for the generation of cationic zirconium alkyls of the type [L$_2$ZrR]$^+$, which are catalytically active (vide-infra) [5,26].

2.5. Preparation of [C$_6$H$_5$C(NC$_3$H$_7$)$_2$](C$_5$Me$_5$)MCl$_2$ (M = Ti (**7**), Zr (**8**)) and [C$_6$H$_5$C(NC$_6$H$_{11}$)$_2$](C$_5$Me$_5$)TiCl$_2$ (**9**)

Another goal of this study was the preparation of mixed-ligand complexes of Ti and Zr containing both pentamethylcyclopentadienyl and the N-alkylated benzamidinate ligands. The reactions between (C$_5$Me$_5$)TiCl$_3$ and (C$_5$Me$_5$)ZrCl$_3$ with Li[C$_6$H$_5$C(NC$_3$H$_7$)$_2$] or Li[C$_6$H$_5$C(NC$_6$H$_{11}$)$_2$] were carried out in THF solution according to Eq. (8). THF is known to be a suitable solvent especially for reactions with (C$_5$Me$_5$)ZrCl$_3$ as it forms the stable monomeric adduct (C$_5$Me$_5$)ZrCl$_3$(THF) [27].

7: M = Ti; R = *i*-Pr
8: M = Zr; R = *i*-Pr
9: M = Ti; R = Cy

(8)
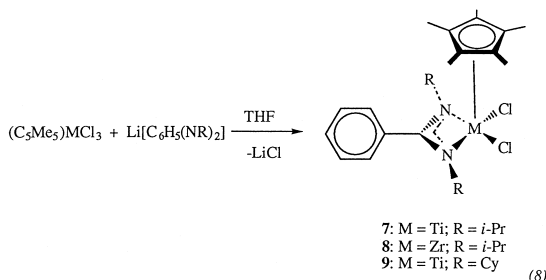
The mixed ligand complexes **7**–**9** were isolated in the form of red (M = Ti) or yellow (M = Zr) crystals. As expected, these complexes exhibit a significantly higher hydrolytic stability as compared to their *N*-trimethylsilyl

substituted counterparts. Crystals of **7**–**9** are stable in air for several days. They are highly soluble in THF or toluene, and moderately soluble in hexane.

2.6. Polymerization activity studies

The catalytic polymerization of ethylene and propylene were studied using the catalytic precursors **1** and **2**. Cationic catalysts were generated by the reaction of the corresponding complexes with methylaluminoxane (MAO) [1]. For the dimethyl analogue of complex **2**, the cationic active species was determined spectroscopically by reacting the dimethyl complex with an excess of MAO or B(C$_6$F$_5$)$_3$ in an NMR tube. The methyl Zr-(CH$_3$)$_2$ signal at 44.3 ppm in the ^{13}C-NMR shifts toward 62.3 ppm in the [Zr-(CH$_3$)]$^+$ similar to other cationic signals found for resembling cyclopentadienyl complexes [2]. Ethylene and propylene polymerizations were carried out under vigorously anaerobic/anhydrous vacuum line conditions, and reactions were quenched after measured time intervals with methanol/HCl solutions prior to polymer collection, washing with pentane and acetone and drying. Polymer microstructure of the obtained high density polyethylene or atactic polypropylene were characterized by ^{13}C NMR using standard analysis [46].

Several interesting trends are evident in the ethylene polymerization data (Table 2). The activity of the catalysts is strongly dependent on the temperature (entries 2, 5 and 8). Thus, raising the temperature from 0 to 60°C induces an increase in catalytic activity by a factor of 15 and lowers the melting point (smaller chains) of

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[1] The polymerization of either ethylene or propylene by complex **6** activated by either MAO or B(C$_6$F$_5$)$_3$ gave similar polymerization results as those obtained for ethylene or propylene with complex **2** and MAO.

[2] For recent reviews on olefin polymerization catalysts, see Refs. [28–34]. For some recent references, see [35–45].

the polymer. Large effects have been also observed for the Al:Zr ratio (compare entries 3–6 or 7–10). Increasing the Al:Zr ratio results in a general increase in the catalytic activities reaching a plateau limit with larger excess of MAO. This leveling behavior obtained by adding large excess of MAO and increasing the ratio Al:Zr is opposite to the behavior found by the analogue cyclopentadienyl early transition metal systems, in which the larger the ratio Al:Zr the larger the catalytic activity is observed [35–53]. This result can be rationalized by the known effects of the cocatalyst concentration catalyzing different possible eliminations, alkyl transfer pathways and other deactivation processes [3]. In addition, the metal effect on these benzamidinate ancillary ligands is shown by comparing the catalytic precursor **1** and **2**. The titanium complex has been found to be a slightly better catalyst than the analogous zirconium complex. This similar behavior has been encountered in the polymerization of ethylene and propylene by bisamido ancillary ligands [56].

The polymerization of propylene to atactic polypropylene by the catalytic complexes **1** and **2** resembles the same features obtained for ethylene. For polypropylene, the proton and carbon spectroscopic analyses of the polymers reveal only vinyl/iso-propyl end groups with no vinylidene/*n*-propyl end groups (characteristic NMR for the obtained polymer structure is given in Section 3) similar to the polymers obtained by $Cp_2^*MMe^+$ (M = Zr, Hf) systems [57,58]. Polymers containing these end-groups may be formed at least from three different theoretical mechanisms. The first, involves an allylic C–H activation of propylene [59], the second, involves a β-methyl elimination [59], and thirdly, a β-hydrogen elimination from a polymer chain in which the last inserted monomer inserts in a 2–1 fashion. The last mechanism in our case can be rejected since no *n*-propyl end groups are observed. Noteworthy to point out, that the

time used for the polymerization was 5 min. Larger polymerization periods of time does not achieve more polymer. This result indicates that besides the β-methyl elimination pathway, which presumably is the major chain termination process, a competitive deactivating pathway is taking place inhibiting polymer formation. We believe that the competitive β-hydrogen elimination pathway from the ancillary ligand is responsible for this deactivation of the catalyst. A simple comparison in the polymerization of either propylene or ethylene, of catalyst **2** with the bis(silylated)benzamidinate zirconium dichloride $[C_6H_5C(NSiMe_3)_2]_2ZrCl_2$ complex [5] in which no β-hydrogens are present at the ancillary ligands, shows that for the latter, the catalytic activity is similar to that observed for complex **2**, though the catalyst is able to polymerize the α-olefins for long periods of time.

It is very interesting to compare some of our results with similar catalytic polymerization systems containing the benzamidinate ancillary ligation. For example, reactions of mixed cyclopentadienyl-benzamidinate titanium dichlorides and a large excess of MAO (Al/Ti = 839) have shown an ethylene catalytic activity of 0.6×10^5 g polymer $mol(Ti)^{-1}$ h^{-1} atm^{-1}. Similar mixed system of zirconium dimethyl with $B(C_6F_5)_3$ as cocatalyst has a smaller activity compared to the corresponding Ti of 1.2×10^4 g polymer $mol(Zr)^{-1}$ h^{-1} atm^{-1}, presumably due to the production of the inert pentafluorophenyl side complex [60,61]. The use of these hard basic benzamidinate ligands replacing both cyclopentadienyl groups stems from the fact that these are electron withdrawing ancillary ligands which should enhance the electrophilic character of the metal center (as found for the methyl signal in the ^{13}C-NMR, 62.3 ppm, of the respectively cationic Zr–Me$^+$ complex). These benzamidinate systems are 4 electron donating groups with 2 coordination sites whereas the cyclopentadienyl ligand is a 6 electron donating and 3 coordination site system. Comparing the results of mixed systems (Zr, Ti)

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[3] For a summary on reaction pathways, see Refs. [54,55].

to those obtained in Table 2, it is evident that two benzamidinate ligation groups have a moderately improved catalytic reactivity. It is important to point out, that both systems have lower catalytic reactivity than the analogous cyclopentadienyl systems for the polymerization of ethylene or propylene $(1 \times 10^7$ and 6×10^6 g mol$(Zr)^{-1}$ h^{-1} atm^{-1}, for ethylene and propylene, respectively [31]) despite the larger catalytic activity which has been observed, for example, in the bis(benzamidinate)yttrium-catalyzed oligomerization of alkynes [4].

The difference in catalytic activity of our 'cationic' complexes compared with the cyclopentadienyl 'cationic' systems can be rationalized by the structural environment of the metal center. Normally, it has been observed that the smaller the angle between the ancillary ligands, the more coordinatively unsaturated the metal center of the complex and the better the catalytic activity observed for the catalyst [4], although, in our case, we have a catalyst with lesser reactivity in the catalytic polymerization of ethylene than the analogous cyclopentadienyl complexes. This activity–structure relationship for complex **2** can be simply illustrated by the fact that the small angle tilted to the back of the molecule $[N(2)–Zr(1)–(N2)' = 89.2 \ (3)°]$ will prevent the approach of the olefin from the back similarly to the cyclopentadienyl case, although the presence of the large angle $N(1)–Zr(1)–N(1)' = 153.5(2)$ with the two isopropyl equatorial groups congest the approach from the side of the molecule, which may induce the low catalytic activity. This side approach is believed to be responsible for the catalytic polymerization activity of the metal center which is governed by the 4 center transition state mechanism [5].

3. Experimental part

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high vacuum $(10^{-5}$ Torr) line, or in a nitrogen filled vacuum atmospheres glove box with a medium capacity recirculator (1–2 ppm O_2). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents were distilled under argon from sodium benzophenone ketyl. Hydrocarbon solvents (toluene-d_8, C_6D_6, hexane) were distilled under nitrogen from Na/K alloy. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable bulbs. Nitrile compounds (Aldrich) were degassed and freshly distilled under argon. NMR spectra were recorded on a Bruker AM 200 spectrometer. Chemical shifts for ^{1}H- and ^{13}C-NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. The NMR experiments were conducted on teflon valve-sealed tubes (J-Young) after vacuum transfer of the solvent in a high vacuum line.

3.1. Reactions of MCl_4 (M = Ti, Zr) with $Li[C_6H_5C(NC_3H_7)_2]$ and $Li[C_6H_5C(NC_6H_{11})_2]$ (general procedure)

To a stirred solution of the given amount of $TiCl_4(THF)_2$ or $ZrCl_4(THF)_2$ in 130 ml THF is added dropwise at room temperature over a period of 15 min a solution of the lithium benzamidinate (molar ratio 1:2) in 100 ml THF. The reaction mixture is stirred overnight at room temperature. The solvent is removed in vacuum, the residue is extracted with 80 ml of toluene and precipitated LiCl is removed by filtration through a thin layer of Celite filter-aid. The clear filtrate is evaporated to dryness, washed

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[4] For some recent references, see [62–65].
[5] For representative theoretical studies on Ziegler Natta polymerizations, see Refs. [66–75].

with hexane (20–30 ml) and dried under vacuum (12 h).

3.2. Dichloro-bis(N,N′-diisopropylbenzamidinato)titanium (IV) (**1**)

The reaction of 6.68 g (20.0 mmol) $TiCl_4(THF)_2$ with 8.41 g (40.0 mmol) $Li[C_6H_5C(NC_3H_7)_2]$ affords 7.12 g (68%) of the wine-red product, m.p. 103°C. Found: C 58.7, H 7.1, N 10.1; calc. for $C_{26}H_{38}Cl_2N_4Ti$ (525.40): C 59.4, H 7.3, N 10.7%. IR: 1636 m, 1342 m, 1217 m, 1170 m, 1157 m, 1137 m, 1075 m, 1014 s, 974 m, 938 w, 919 w, 892 w, 846 w, 702 m, 541 w, 496 w, 435 w cm^{-1}. MS: m/z 524 [M, 2%], 509 [M-CH_3, 7%], 321 [M-$C_6H_5C(NC_3H_7)_2$, 14%], 203 [$C_6H_5C(NC_3H_7)_2$, 43%], 146 [$C_6H_5C(NC_3H_7)$, 25%], 104 [C_6H_5CNH, 100%]. ^1H NMR (THF-d_8, 200.13 MHz): δ 7.55 (m, 6 H, C_6H_5), 7.28 (m, 4 H, C_6H_5), 3.45 [sept, 4 H, CH(CH$_3$), $^3J_{H-H} = 7.5$ Hz], 1.35 [d, 24 H, CH(CH_3)$_2$, $^3J_{H-H} = 7.5$ Hz] ppm. ^{13}C NMR (CDCl$_3$): δ 176.9 [$C_6H_5C(NC_3H_7)_2$], 129.9 (C_6H_5, C_{ipso}), 129.6 (C_6H_5), 128.7 (C_6H_5), 128.5 (C_6H_5), 126.5 (C_6H_5), 126.0 (C_6H_5), 52.4 [CH(CH$_3$)$_2$], 23.9 [CH(CH$_3$)$_2$] ppm.

3.3. Dichloro-bis(N,N′-diisopropylbenzamidinato)zirconium (IV) (**2**)

The reaction of 7.54 g (20.0 mmol) $ZrCl_4(THF)_2$ with 8.41 g (40.0 mmol) $Li[C_6H_5C(NC_3H_7)_2]$ gave 6.78 g (60%) of a pale yellow, crystalline powder, m.p. 85°C (dec.). Found: C 54.0, H 6.3, N 9.5; calc. for $C_{26}H_{38}Cl_2N_4Zr$ (568.75): C 54.9, H 6.7, N 9.9%. IR: 3067 m, 1639 m, 1578 w, 1507 m, 1417 s, 1343 s, 1219 m, 1172 m, 1140 m, 1127 m, 1075 m, 1016 m, 974 w, 944 w, 914 w, 848 w, 777 s, 738 m, 702 s, 484 w, 418 w cm^{-1}. MS: m/z 203 [$C_6H_5C(NC_3H_7)_2$, 25%], 161 [$C_6H_5CNH(NC_3H_7)$, 12%], 146 [$C_6H_5C(NC_3H_7)$, 7%], 132 [$C_6H_5C(NC_2H_5)$, 17%], 104 [C_6H_5CNH, 100%], 58 [HNC_3H_7,

45%]. ^1H NMR (THF-d_8): δ 7.55 (m, 6 H, C_6H_5), 7.25 (m, 4 H, C_6H_5), 3.30 [sept, 4 H, CH(CH$_3$)$_2$, $^3J_{H-H} = 7.2$ Hz], 1.28 [d, 24 H, CH(CH_3)$_2$, $^3J_{H-H} = 7.2$ Hz] ppm. ^{13}C NMR (THF-d_8): δ 180.8 [$C_6H_5C(NC_3H_7)_2$], 131.6 (C_6H_5, C_{ipso}), 130.4 (C_6H_5), 129.8 (C_6H_5), 126.8 (C_6H_5), 50.4 [CH(CH$_3$)$_2$], 25.0 [CH(CH$_3$)$_2$] ppm.

Due to some sensitivity of the compound to moisture and oxygen, a suitable crystal for X-ray analysis was placed inside a glovebox into Kel-F Oil (Voltalef). Then, it was mounted on the four cycle diffractometer where it met a cold stream of nitrogen at 223 K. Reflections were collected on a Siemens P4 automated four cycle diffractometer. Intensities were corrected in the usual way except for absorption. The structure was solved by direct methods, and refined, based on F^2, by full matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic temperature coefficients. The hydrogen atoms were included by use of a riding model and refined isotropically. The d(C–H) used was 0.95 Å for the aromatic and 0.98 Å for the methyl hydrogens. Preliminary data, measurement conditions and structure refinement are summarized in Table 3. Final atomic coordinates are given in Table 4. Additional material available from the Cambridge Crystallographic Data Center comprises thermal parameters hydrogen coordinates and the structural factors.

3.4. Dichloro-bis(N,N′-dicyclohexylbenzamidinato)titanium (IV) (**3**)

From 5.27 g (15.8 mmol) $TiCl_4(THF)_2$ and 9.18 g (31.8 mmol) $Li[C_6H_5C(NC_6H_{11})_2]$ are isolated 6.87 g (64%) of a wine-red, crystalline solid, m.p. 128°C (dec.). Found: C 65.8, H 7.5, N 7.8; calc. for $C_{38}H_{34}Cl_2N_4Ti$ (685.66): C 66.6, H 7.9, N 8.2%. IR: 2122 s, 1639 m, 1346 s, 1212 w, 1152 m, 1074 s, 1057 s, 989 m, 919 w, 889 w, 843 w, 774 m, 702 w, 669 w, 533 w, 494 w, 439 w cm^{-1}. MS: m/z 686 [M, 8%], 403 [M-$C_6H_5C(NC_6H_{11})_2$, 10%], 283 [$C_6H_5C(NC_6H_{11})_2$, 100%], 201

$[C_6H_5CNH(NC_6H_{11})$, 22%], 104 $[C_6H_5CNH$, 59%]. ^1H NMR (THF-d_8): δ 7.08–7.61 (m, 10 H, C_6H_5) 3.02 (m, 4 H, CHC$_5H_{10}$), 0.85–2.15 (m, 40 H, CHC_5H_{10}) ppm.

3.5. Dichloro-bis(N,N'-dicyclohexylbenzamidinato)zirconium (IV) (**4**)

Treatment of 6.49 g (17.2 mmol) ZrCl$_4$(THF)$_2$ with 9.97 g (34.3 mmol) of Li[C$_6$H$_5$C(NC$_6$H$_{11}$)$_2$] affords 8.02 g (64%) of the pale yellow product, m.p. 118°C. Found: C 61.9, H 6.9, N 7.5; calcd. for C$_{38}$H$_{54}$Cl$_2$N$_4$Zr (729.01): C 62.6, H 7.5, N 7.7%. IR: 3271 m, 2118 m, 1635 w, 1605 m, 1529 m, 1349 w, 1221 w, 1153 m, 1076 m, 991 w, 930 w, 891 w, 844 w, 776 m, 705 w, 670 w, 525 w, 491 w, 434 w cm^{-1}. MS: m/z 283 [C$_6$H$_5$C(NC$_6$H$_{11}$)$_2$, 88%], 201 [C$_6$H$_5$CNH(NC$_6$H$_{11}$), 84%], 121 [C$_6$H$_5$C(NH$_2$)$_2$, 55%], 104 [C$_6$H$_5$CNH, 100%], 98 [HNC$_6$H$_{11}$, 48%]. ^1H NMR (THF-d_8): δ 7.08–7.61 (m, 10 H, C$_6$H$_5$), 2.80 (m, 4 H, CHC$_5$H$_{10}$), 0.82–2.17 (m, 40 H, CHC_5H_{10}) ppm. ^{13}C NMR (CDCl$_3$): δ 177.8 [C$_6$H$_5$$C$(NC$_6H_{11}$)$_2$], 139.8 (C$_6H_5$, C$_{ipso}$), 132.0 (C$_6H_5$), 129.8 (C$_6H_5$), 128.9 (C$_6H_5$), 128.7 (C$_6H_5$), 126.1 (C$_6H_5$), 58.1 ($CHC_5H_{10}$), 34.6 (CH$C_5H_{10}$), 25.8 (CH$C_5H_{10}$), 24.7 (CH$C_5H_{10}$) ppm.

3.6. Dichloro-bis[N,N'-dicyclohexyl-2,4,6-tris(trifluoromethyl)benzamidinato]zirconium (IV) (**5**)

The reaction of 3.47 g (9.2 mmol) ZrCl$_4$(THF)$_2$ with 9.07 g (18.3 mmol) Li[(CF$_3$)$_3$C$_6$H$_2$C(NC$_6$H$_{11}$)$_2$] affords 2.46 g (24%) of a cream-colored solid, m.p. 161°C (dec.). Found: C 45.9, H 4.0, N 4.3; calc. for C$_{44}$H$_{48}$Cl$_2$F$_{18}$N$_4$Zr (1136.99): C 46.5, H 4.3, N 4.9%. IR: 2122 w, 1652 m, 1605 w, 1583 w, 1411 m, 1301 m, 1281 m, 1204 m, 1152 s, 912 w, 891 w, 870 w, 685 w, 538 w, 465 w cm^{-1}. MS: m/z 488 [(CF$_3$)$_3$C$_6$H$_2$C(NC$_6$H$_{11}$)$_2$, 10%], 419 [(CF$_3$)$_2$C$_6$H$_2$C(NC$_6$H$_{11}$)$_2$, 10%], 325 [(CF$_3$)$_3$C$_6$H$_2$C(NH$_2$)$_2$, 71%], 83 [C$_6$H$_{11}$, 12%]. ^1H NMR (THF-d$_8$): δ 8.59 (s, 4 H, C$_6$H$_2$),

4.62 (m, 2 H, CHC$_5$H$_{10}$), 2.85 (m, 2 H, CHC$_5$H$_{10}$), 0.91–2.25 (m, 40 H, CHC_5H_{10}) ppm. ^{13}C NMR (THF-d_8): δ 155.2 [s, (CF$_3$)$_3$C$_6$H$_2$C(NC$_6$H$_{11}$)$_2$], 140.0 [s, (CF$_3$)$_3$C$_6$H$_2$, C$_{ipso}$], 135.5 (q, p-C$_6$H$_2$, $^2J_{C-F}$ = 32.4 Hz), 132.3 (q, o-C$_6$H$_2$, $^2J_{C-F}$ = 32.4 Hz), 129.9 (q, m-C$_6$H$_2$, $^3J_{C-F}$ = 6.8 Hz), 123.7 (q, CF$_3$, $^1J_{C-F}$ = 274.5 Hz), 58.8 (s, CHC_5H$_{10}$), 54.0 (s, CHC_5H$_{10}$), 32.1 (s, CHC_5H$_{10}$), 26.3 (s, CHC_5H$_{10}$), 25.9 (s, CHC_5H$_{10}$) ppm. ^{19}F NMR (THF-d$_8$, 235.32 MHz): δ −57.5 Hz (s, 12 F, o-CF$_3$), −63.3 Hz (s, 6 F, p-CF$_3$) ppm.

3.7. Bis(N,N'-dicyclohexylbenzamidinato)dimethylzirconium (IV) (**6**)

3.0 g (4.1 mmol) [C$_6$H$_5$C(NC$_6$H$_{11}$)$_2$]$_2$ZrCl$_2$ (**4**) is suspended in 50 ml of diethylether and 0.27 g (12.4 mmol) methyllithium in 40 ml diethylether is added dropwise at −20°C. The mixture is stirred for another 15 min at −20°C and allowed to warm up to room temperature overnight. The solvent is completely removed in vacuo, the residue is redissolved in pentane (30 ml) and the resulting solution is filtered through a thin layer of Celite filter aid in order to remove insoluble particles. Evaporation of the filtrate to dryness affords 1.67 g (59%) of a yellow crystalline solid, m.p. 135°C. Found: C 69.0, H 8.2, N 7.6; calc. for C$_{40}$H$_{60}$N$_4$Zr (688.17): C 69.8, H 8.8, N 8.1%. IR: 3438 w, 3060 m, 1638 m, 1578 m, 1347 vs, 1311 s, 1212 m, 1153 s, 1100 s, 1074 s, 990 m, 953 m, 918 w, 889 w, 775 m, 702 m, 666 w, 633 w, 624 w, 490 w, 430 w cm^{-1}. MS: m/z 283 [C$_6$H$_5$C(NC$_6$H$_{11}$)$_2$, 100%], 201 [C$_6$H$_5$CNH(NC$_6$H$_{11}$), 91%], 121 [C$_6$H$_5$C(NH$_2$)$_2$, 74%], 104 [C$_6$H$_5$CNH, 90%], 98 [HNC$_6$H$_{11}$, 50%]. ^1H NMR (C$_6$D$_6$): δ 7.00–7.25 (m, 10 H, C$_6$H$_5$), 3.30 (m, 2 H, CHC_5H$_{10}$), 2.95 (m, 2 H, CHC_5H$_{10}$), 0.81–2.25 (m, 40 H, CHC_5H$_{10}$), 0.28 (s, 6 H, CH$_3$) ppm. ^{13}C NMR (C$_6$D$_6$): δ 175.5 [C$_6$H$_5$C(NC$_6$H$_{11}$)$_2$], 137.7 (C$_6$H$_5$, C$_{ipso}$), 130.0 (C$_6$H$_5$), 126.6 (C$_6$H$_5$), 126.4 (C$_6$H$_5$), 57.0 (CHC$_5$H$_{10}$), 49.1 (CH$_3$), 36.4 (CHC_5H$_{10}$), 27.2 (CHC_5H$_{10}$), 26.7 (CHC_5H$_{10}$) ppm.

3.8. Reactions of $(C_5Me_5)MCl_3$ $(M = Ti, Zr)$ with $Li[C_6H_5C(NC_6H_{11})_2]$ and $Li[C_6H_5C(NC_3H_7)_2]$ (general procedure)

To a solution of the given amount of $(C_5Me_5)TiCl_3$ or $(C_5Me_5)ZrCl_3$ in 70 ml THF is added dropwise at 0°C the lithium benzamidinate, dissolved in 30 ml THF. After warming to room temperature the reaction mixture is stirred for another 24 h. The solvent is completely removed in vacuo, the residue is redissolved in toluene (70 ml) and filtered through a thin layer of Celite. After evaporation of the filtrate to dryness, the residue is washed with hexane and dried under vacuum (12 h).

3.9. Dichloro-(N,N′-diisopropylbenzamidinato)-(η^5-pentamethylcyclopentadienyl)titanium (IV) (7)

From 0.87 g (3.0 mmol) $(C_5Me_5)TiCl_3$ and 0.63 g (3.0 mmol) $Li[C_6H_5C(NC_3H_7)_2]$ are isolated 0.38 g (28%) of the orange product, m.p. 135°C (dec.). Found: C 59.3, H 7.0, N 5.6; calc. for $C_{23}H_{34}Cl_2N_2Ti$ (457.33): C 60.4, H 7.5, N 6.1%. IR: 1636 s, 1312 m, 1113 m, 702 m, 620 m, 452 m, 398 m cm^{-1}. MS: m/z 457 [M, 1%], 259 [$(C_5Me_5)TiCl_2$, 8%], 203 [$C_6H_5C(NC_3H_7)_2$, 6%], 135 [C_5Me_5, 100%], 105 [$C_6H_5CNH_2$, 24%]. ^{1}H NMR (THF-d$_8$, 200.13 MHz): δ 7.55 (m, 5 H, C_6H_5), 3.42 [sept, 2 H, CH(CH$_3$)$_2$, $^3J_{H-H}$ = 6.3 Hz], 2.27 [s, 15 H, C_5(CH$_3$)$_5$], 1.35 [d, 12 H, CH(CH_3)$_2$, $^3J_{H-H}$ = 6.3 Hz] ppm. ^{13}C NMR (THF-d$_8$): δ 162.1 [$C_6H_5C(NC_3H_7)_2$], 134.6 [C_5(CH$_3$)$_5$], 132.4 (C_6H_5, C_{ipso}), 130.7 (C_6H_5), 129.8 (C_6H_5), 129.0 (C_6H_5), 128.1 (C_6H_5), 127.9 (C_6H_5), 48.0 [CH(CH$_3$)$_2$], 23.5 [CH(CH$_3$)$_2$], 13.5 [C_5(CH$_3$)$_5$] ppm.

3.10. Dichloro-(N,N′-diisopropylbenzamidinato)-(η^5-pentamethylcyclopentadienyl)zirconium (IV) (8)

The reaction of 0.87 g (2.5 mmol) $(C_5Me_5)ZrCl_3$ with 0.53 g (2.5 mmol) $Li[C_6H_5C(NC_3H_7)_2]$ yields 0.39 g (33%) yel-

low crystals, m.p. 75°C. Found: C 54.1, H 6.2, N 5.2; calc. for $C_{23}H_{34}Cl_2N_2Zr$ (500.67): C 55.2, H 6.9, N 5.6%. IR: 1635 s, 1207 w, 974 m, 937 w, 919 w, 890 w, 674 m, 485 m cm^{-1}. MS: m/z 295 [$(C_5Me_5)ZrCl_2$, 18%], 203 [$C_6H_5C(NC_3H_7)_2$, 20%], 104 [C_6H_5CNH, 100%]. ^{1}H NMR (CDCl$_3$, 200.13 MHz): δ 7.60 (m, 3 H, C_6H_5), 7.30 (m, 2 H, C_6H_5), 3.20 [sept, 2 H, CH(CH$_3$)$_2$, $^3J_{H-H}$ = 6.5 Hz], 2.07 [s, 15 H, C_5(CH$_3$)$_5$], 1.19 [d, 12 H, CH(CH_3)$_2$, $^3J_{H-H}$ = 6.5 Hz] ppm. ^{13}C NMR (CDCl$_3$): δ 164.0 [$C_6H_5C(NC_3H_7)_2$], 132.0 (C_6H_5, C_{ipso}), 129.9 [C_5(CH$_3$)$_5$], 127.9 (C_6H_5), 127.5 (C_6H_5), 127.0 (C_6H_5), 126.4 (C_6H_5), 125.9 (C_6H_5), 48.2 [CH(CH$_3$)$_2$], 23.1 [CH(CH$_3$)$_2$], 13.3 [C_5(CH$_3$)$_5$] ppm.

3.11. Dichloro-(N,N′-dicyclohexylbenzamidinato)-(η^5-pentamethylcyclopentadienyl)titanium (IV) (9)

Treatment of 0.87 g (3.0 mmol) $(C_5Me_5)TiCl_3$ with 0.87 g (3.0 mmol) $Li[C_6H_5C(NC_6H_{11})_2]$ affords 0.56 g (36%) of an orange crystalline solid, m.p. 159°C (dec.). Found: C 63.8, H 7.1, N 4.7; calc. for $C_{29}H_{42}Cl_2N_2Ti$ (537.46): C 64.8, H 7.9, N 5.2%. IR: 1635 s, 1591 m, 1064 m, 978 w, 959 w, 892 w, 844 w, 772 s, 746 s, 665 w, 621 w, 452 w, 397 w cm^{-1}. MS: m/z 283 [$C_6H_5C(NC_6H_{11})_2$, 4%], 254 [$(C_5Me_5)TiCl_2$, 6%], 135 [C_5Me_5, 15%], 98 [HNC_6H_{11}, 12%], 83 [C_6H_{11}, 28%]. ^{1}H NMR (THF-d$_8$, 200.13 MHz): δ 7.52 (m, 5 H, C_6H_5), 3.21 (m, 2 H, CHC$_5$H$_{10}$), 2.21 [s, 15 H, C_5(CH$_3$)$_5$], 0.82–2.38 (m, 20 H, CHC$_5$H$_{10}$) ppm. ^{13}C NMR (THF-d$_8$): δ 158.5 [$C_6H_5C(NC_6H_{11})_2$], 141.2 (C_6H_5, C_{ipso}), 134.5 [C_5(CH$_3$)$_5$], 130.4 (C_6H_5), 129.8 (C_6H_5), 129.6 (C_6H_5), 128.8 (C_6H_5), 126.0 (C_6H_5), 55.6 (CHC$_5$H$_{10}$), 32.4 (CHC_5H$_{10}$), 26.3 (CHC_5H$_{10}$), 23.4 (CHC_5H$_{10}$), 13.4 [C_5(CH$_3$)$_5$] ppm.

3.12. Ethylene and propylene polymerizations

General procedure: A 100 ml glass reactor with a strong magnetic stirrer, flame dried under

vacuum for few hours, was charged with 5 mg of the catalyst and a specific amount of MAO inside the glovebox. The reactor was connected to a high vacuum line and 20 ml of toluene was condensed by vacuum tranfer. After equilibration of the temperature and under strong stirring, ethylene or propylene (purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column) were introduced into the reactor and mantained at atmospheric pressure by means of a manometer. Polymerizations were quenched by introducing 30 ml of methanol/HCl. Polyethylene was filtered out washed with water, pentane and acetone. For polypropylene, the organic layer was separated and washed with water, treated with molecular sieves and dried under vacuum 0.001 mm Hg at 60°C for few hours.

For polypropylene, the ^{13}C NMR shows only the β-methyl elimination polymer signals
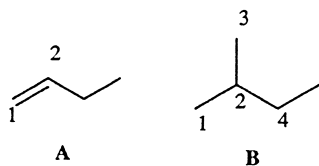
The relevant signals for the determination are: δ (C_6D_8) 135.7 (A_2), 114.3 (A_1), 46.2 (B_4), 24.5 (B_2), 21.5 (B_3), 20.5 (B_1). No signals were observed at 142, 109.5 ppm from a vinylidene end group or at 12.5 ppm for the *n*-propyl group.

Acknowledgements

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