

# Catalytic polymerization of propylene by heterobimetallic bridged early/late transition metal complexes

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## Abstract

The polymerization of propylene was studied with a series of dinuclear early transition metal zirconocene-late transition metal complexes bridged by phosphido and arsenido moieties of general formula  $[(\eta^5\text{-C}_5\text{H}_4\text{R}'')_2\text{Zr}\{\mu\text{-ERR}'\}_2\text{M}(\text{CO})_n]$  (E = P, R = R' = SiMe<sub>3</sub>, R'' = H, M = Mo, n = 4 (1); E = P, R = R' = SiMe<sub>3</sub>, R'' = H, M = Ni, n = 2 (2); E = As, R = R' = SiMe<sub>3</sub>, R'' = H, M = Cr, n = 4 (3); E = P, R = H, R' = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, R'' = Me, M = Mo, n = 4 (4); E = P, R = H, R' = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, R'' = Me, M = Cr, n = 4 (5)), as well as with the corresponding monometallic zirconocene precursor complexes of the type  $[(\eta^5\text{-C}_5\text{H}_4\text{R}'')_2\text{Zr}(\text{ERR}')_2]$  (E = P, R = R' = SiMe<sub>3</sub>, R'' = H (6); E = P, R = H, R' = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, R'' = H (7)) and  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{Zr}(\text{ERR}')\text{Cl}]$  (E = P, R = H, R' = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (8)). The active cationic species were generated treating the complexes with an excess of methylalumoxane (MAO). The catalytic activity was found to be strongly dependent on temperature and catalyst/MAO ratio. © 1998 Elsevier Science B.V.

## 1. Introduction

Heterobimetallic compounds incorporating both early and late transition metals are of current interest due to their relationship to heterogeneous Fischer–Tropsch catalysts and, recently, as active catalysts for the Ziegler–Natta polymerization of ethylene [1]. Most of these catalysts have low-valent late transition metals attached directly or through bridging ligands to a high-valent early transition metal, thereby the

degree of interaction between the metals has profound effects on the activity of the resulting catalysts. For example, the term ‘strong metals interaction’ (SMI) has been used to describe the drastic decrease in the ability of noble metals of groups 8–10 to chemisorb hydrogen when they are supported on titanium oxide ([2] and references therein).

Recently, heterometallic complexes have been the subject of several reviews. Complexes containing both early and late transition metals often contain bridging ligands that result in stable compounds in which the two different metals are kept in proximity ([3–5] and references therein).

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Recently, advances in early/late bridged transition metal complexes can be attributed to the beneficial influence of the early transition metal supporting ligation on the catalytic properties of the late transition metal towards organic substrates ([6–10] and references therein). In principle, each metal center in such a binuclear compound can undergo reactions characteristic of a mononuclear transition-metal complex. Thus, a high-valent early transition metal could be active in processes such as alkene oxidation or metathesis, while an adjacent low-valent transition metal could undergo oxidative addition, reductive elimination and insertion. Likewise, cooperative reactivity could stem from the possibility for the electron-poor early transition metal and the electron-rich late transition metal to create an ideal environment for heterolytic bond cleavage of polar substrates. Although many early/late transition metal heterobimetallic complexes have been prepared, few of them have shown a truly cooperative synergistic reactivity with organic substrates [11–13]. The observed reactivity has been shown to occur at a single metal center, presumably because the large distance between the metal centers does not permit any synergistic effect. The reactivity is normally found at the late transition metal center due to the coordinative saturation of the early transition metal center. Nevertheless, some cases have been reported in which an influence of the early transition metal on the reactivity of the late transition metal center is found [14–16]. Only in a few reactions has participation of both metals in a reaction with an organic substrate been observed [17–19].

We report here a comprehensive study in which a large effect is found for the late transition moiety on the catalytic activity of the electron-poor early transition metal in the polymerization of propylene, employing a series of dinuclear early/late phosphido- and arsenido-bridged zirconocene-late transition metal complexes of general formula  $[(\eta^5\text{-C}_5\text{H}_4\text{R}'')_2\text{Zr}\{\mu\text{-ERR}'\}_2\text{M}(\text{CO})_n]$  (E = P, R = R' = SiMe<sub>3</sub>, R'' = H, M = Mo, *n* = 4 (1); E = P, R = R' = SiMe<sub>3</sub>,

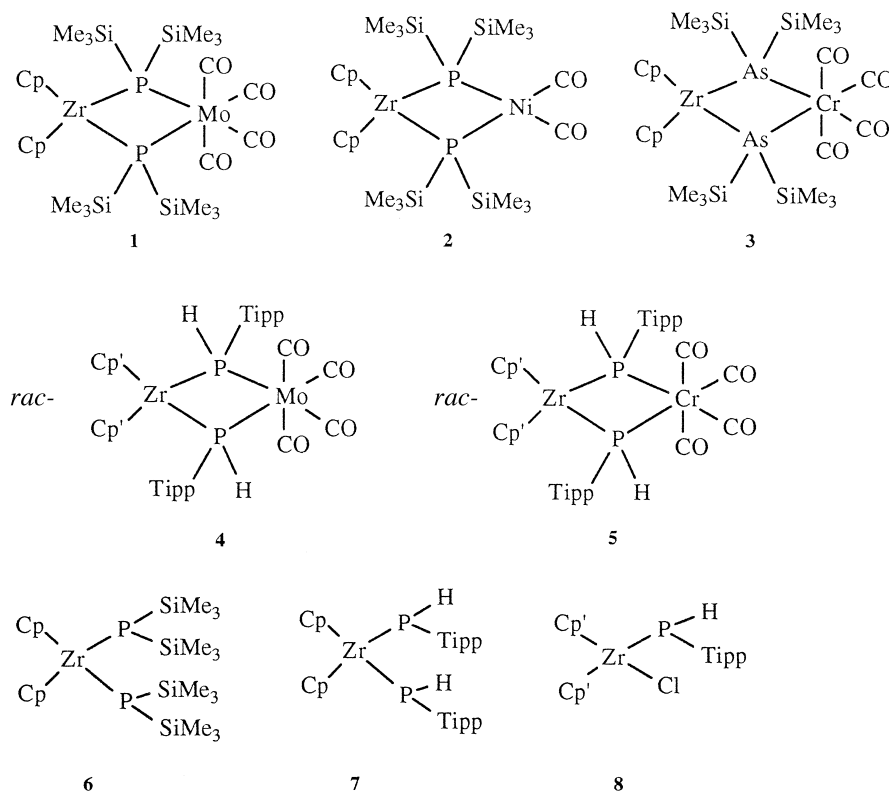
R'' = H, M = Ni, *n* = 2 (2); E = As, R = R' = SiMe<sub>3</sub>, R'' = H, M = Cr, *n* = 4 (3); E = P, R = H, R' = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, R'' = Me, M = Mo, *n* = 4 (4); E = P, R = H, R' = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, R'' = Me, M = Cr, *n* = 4 (5)) along with a comparison to the corresponding monometallic zirconocene precursor complexes of the type  $[(\eta^5\text{-C}_5\text{H}_4\text{R}'')_2\text{Zr}(\text{ERR}')_2]$  (E = P, R = R' = SiMe<sub>3</sub>, R'' = H (6); E = P, R = H, R' = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, R'' = H (7)) and  $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{Zr}(\text{ERR}')\text{Cl}$  (E = P, R = H, R' = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (8)). For each complex, the active cationic species was obtained by using an excess of methylalumoxane (MAO). The electronic effect of the electron-rich late transition metal moiety on the cationic zirconocene has been correlated with the observed polymerization activity.

In addition, an attempt was made to initiate the propylene polymerization by employing the weakly coordinating salt tributylammonium tetrakis(pentafluorophenyl)borate  $[(\text{C}_6\text{F}_5)_4\text{B}]^-\text{[NH}(n\text{-Bu})_3]^+$  with complex 1. However, this precatalyst/ $(\text{C}_6\text{F}_5)_4\text{B}^-$  system proved to be inactive as a polymerization catalyst, affording polymerization reactivity only after the addition of equimolar amounts of AlMe<sub>3</sub> ([20–36] and references cited therein).

## 2. Results and discussion

The complexes used in this study for the polymerization of propylene are shown in Fig. 1.

Complexes 1–8 are stable compounds with no catalytic reactivity towards olefins in the presence of dihydrogen or/and carbon monoxide, due to the electronic and coordinative saturation of both early and late transition metals. However these complexes can be activated to give coordinatively unsaturated cationic zirconocenes by a strong Lewis acid such as methylalumoxane (MAO). These activated complexes were found to be active catalysts for the



Tipp = 2, 4, 6, tri(*i*-propyl)phenyl, Cp' =  $\eta^5$ -MeC<sub>5</sub>H<sub>4</sub>

Fig. 1. Early-late heterodinuclear bridged phosphido- and arsenido-complexes and monophosphido- or bis(phosphido)-zirconocene complexes as efficient precatalysts for the atactic polymerization of propylene.

polymerization of propylene. The heterodinuclear complexes 1–5 are excellent examples of early/late heterobimetallic bridged phosphido/arsenido complexes used as catalytic precursors in polymerization reactions in which the electron-rich late transition metal influences the oxophilic electron-poor early transition metal.

The catalytic polymerization of propylene was studied with the precatalysts 1–8. Active cationic catalysts were generated by treating the corresponding complexes with excess MAO. 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 and drying. The polymer microstructure of the obtained atactic polypropy-

lene was characterized by standard <sup>13</sup>C-NMR analysis [37].

### 2.1. Catalytic polymerization of propylene promoted by the heterodinuclear complexes 1–5

Several trends are evident in the propylene polymerization data for the heterodinuclear early/late transition metal complexes 1–5 (Table 1). The catalyst activity is strongly dependent on temperature (entries 1, 5, 8; 2, 6, 9; 22, 24, 26). Thus, raising the temperature from 273 to 303 K for a catalyst/MAO ratio of 1:1350 causes an increase in the catalytic activity by a factor of 2, 3, 12 and 16 for complexes 1, 2, 3, and 5, respectively. A further temperature increase to 333 K produces a small decrease in catalytic activity (except for complex 2). Large effects have also been observed for the Al:Zr

Table 1  
Activity data for the polymerization of propylene with heterobimetallic complexes 1–5

Entry	Catalyst	[catal] <sup>a,b</sup> (mmol)	<i>T</i> (°K)	MAO <sup>c</sup> (mmol)	Cat/MAO ratio	Activity <sup>d</sup>
1	<b>1</b>	$6.38 \times 10^{-3}$	273	6.38	1:1000	$3.1 \times 10^4$
2	<b>1</b>	$6.38 \times 10^{-3}$	273	8.62	1:1350	$3.8 \times 10^4$
3	<b>1</b>	$6.38 \times 10^{-3}$	273	17.24	1:2700	$6.6 \times 10^4$
4	<b>1</b>	$6.38 \times 10^{-3}$	303	4.79	1:750	$1.5 \times 10^5$
5	<b>1</b>	$6.38 \times 10^{-3}$	303	6.38	1:1000	$1.2 \times 10^5$
6	<b>1</b>	$6.38 \times 10^{-3}$	303	8.62	1:1350	$6.6 \times 10^4$
7	<b>1</b>	$6.38 \times 10^{-3}$	303	17.24	1:2700	$5.2 \times 10^4$
8	<b>1</b>	$6.38 \times 10^{-3}$	333	6.38	1:1000	$5.0 \times 10^4$
9	<b>1</b>	$6.38 \times 10^{-3}$	333	8.62	1:1350	$5.3 \times 10^4$
10	<b>1</b>	$6.38 \times 10^{-3}$	333	17.24	1:2700	$6.7 \times 10^4$
11	<b>2</b>	$7.24 \times 10^{-3}$	273	8.62	1:1350	$8.3 \times 10^3$
12	<b>2</b>	$7.24 \times 10^{-3}$	303	6.38	1:1000	$1.1 \times 10^4$
13	<b>2</b>	$7.24 \times 10^{-3}$	303	8.62	1:1350	$2.2 \times 10^4$
14	<b>2</b>	$7.24 \times 10^{-3}$	303	17.24	1:2700	$8.4 \times 10^3$
15	<b>2</b>	$7.24 \times 10^{-3}$	333	8.62	1:1350	$5.0 \times 10^4$
16	<b>3</b>	$6.03 \times 10^{-3}$	273	8.62	1:1350	$4.7 \times 10^3$
17	<b>3</b>	$6.03 \times 10^{-3}$	303	6.38	1:1000	$4.3 \times 10^4$
18	<b>3</b>	$6.03 \times 10^{-3}$	303	8.62	1:1350	$5.6 \times 10^4$
19	<b>3</b>	$6.03 \times 10^{-3}$	303	17.24	1:2700	$6.1 \times 10^4$
20	<b>3</b>	$6.03 \times 10^{-3}$	333	8.62	1:1350	$2.8 \times 10^4$
21	<b>4</b>	$5.56 \times 10^{-3}$	303	17.24	1:2700	$3.2 \times 10^4$
22	<b>5</b>	$5.84 \times 10^{-3}$	273	8.62	1:1350	$2.6 \times 10^3$
23	<b>5</b>	$5.84 \times 10^{-3}$	303	6.38	1:1000	$9.3 \times 10^4$
24	<b>5</b>	$5.84 \times 10^{-3}$	303	8.62	1:1350	$4.2 \times 10^4$
25	<b>5</b>	$5.84 \times 10^{-3}$	303	17.24	1:2700	$1.2 \times 10^4$
26	<b>5</b>	$5.84 \times 10^{-3}$	333	8.62	1:1350	$2.8 \times 10^4$

<sup>a</sup>In 30 ml toluene.

<sup>b</sup>Atmospheric pressure.

<sup>c</sup>Methylalumoxane, solvent removed from a 20 wt% solution in toluene (Witco) at 25°C/10<sup>-6</sup> Torr.

<sup>d</sup>Grams total polymer/mol Zr (mol l<sup>-1</sup>) h atm.

ratio (compare entries 1–3, 4–7, 8–10, etc.). Increasing the Al:Zr ratio results in a small decrease or a plateau in the catalytic activity. Hence, in general, the smaller the MAO/catalyst ratio used, the higher the catalytic activity (limit  $\approx$  1:1000).

This behavior is opposite to that normally exhibited by early transition metal metallocene complexes such as for complex **8** (vide infra), but is similar to the behavior observed for benzamidinate cationic zirconium complexes [38], bis(amido) titanium and zirconium complexes [39], bis(phosphido)-zirconocene complexes such as **6** and **7** (vide infra), or heterodinuclear early/late transition metal complexes in the polymerization of ethylene [1]. This behavior can be simply rationalized by the effect of the cocatalyst concentration on the catalysis of vari-

ous possible elimination routes, alkyl transfer pathways and other deactivation processes [26,27,40–42].

On increasing the donor interaction of the late transition metal towards the oxophilic center, lower catalytic reactivity towards the olefin was obtained. The increased electron density at the Zr atom due to the late transition metal  $M(d^{10}) \Rightarrow Zr(d^0)$  donor interactions can be seen in the <sup>1</sup>H-NMR Cp signals, which are shifted to higher fields on going from the monometallic zirconocenes to the heterobimetallic complexes (Table 2). Noteworthy to point out that the NMR chemical shifts for the complexes have been measured by dissolving the different complexes in the same solvent (C<sub>6</sub>D<sub>6</sub>) to avoid coordinative solvent effects. Moreover, no major differences are found in the structure of the

Table 2

<sup>1</sup>H-NMR data of compounds **1–8** (region of the cyclopentadienyl protons only)<sup>a</sup>

Compound	$\delta$ /ppm	Ref.
Cp <sub>2</sub> Zr{P(SiMe <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> ( <b>6</b> )	6.03 t (10H), <sup>3</sup> J <sub>PH</sub> = 1.0 Hz	[43]
Cp <sub>2</sub> Zr{ $\mu$ -P(SiMe <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> Mo(CO) <sub>4</sub> ( <b>1</b> )	5.35 s (10H)	[44]
Cp <sub>2</sub> Zr{ $\mu$ -P(SiMe <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> Ni(CO) <sub>2</sub> ( <b>2</b> )	5.43 s (10H)	[1]
Cp <sub>2</sub> Zr{ $\mu$ -As(SiMe <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> Cr(CO) <sub>4</sub> ( <b>3</b> )	5.36 s (10H)	[44]
<i>rac</i> -Cp <sub>2</sub> Zr( $\mu$ -PHTipp) <sub>2</sub> Mo(CO) <sub>4</sub> ( <b>4</b> )	4.75 br (2H), 4.99 br (2H), 5.10 m (2H), 5.29 m (2H)	[46]
<i>rac</i> -Cp <sub>2</sub> Zr( $\mu$ -PHTipp) <sub>2</sub> Cr(CO) <sub>4</sub> ( <b>5</b> )	4.77 br (2H), 5.07 br (4H), 5.32 m (2H)	[46]
Cp <sub>2</sub> Zr(PHTipp) <sub>2</sub> ( <b>7</b> )	5.57 s (10H)	[46]
Cp <sub>2</sub> ZrCl(PHTipp) ( <b>8</b> )	5.25 br (2H), 5.38 br (2H), 5.74 m (2H), 5.99 m (2H)	[45]

<sup>a</sup> Solvent = C<sub>6</sub>D<sub>6</sub>.

different bridged complexes and monomeric complexes allowing us to compare the difference in electron density around the metal center as observed by the cyclopentadienyl ligands.

In addition, the electronic effect imparted by the late-transition metal on the early component is also clearly shown by comparing the CO stretching bands in the IR spectrum (Table 3). In comparing the frequency of the carbonyl moieties after addition of MAO with the reactivity of complexes **1**, **2** and **3**, the molybdenum moiety of complex **1** is more electronegative (red shift) than that of the chromium moiety of **3**, indicating a weaker donor interaction with the oxophilic center, resulting in a more reactive complex. The electronic effect of the late transition moiety on complex **2**, lies between those of complexes **1** and **3**. Furthermore, for complexes

**4** and **5**, no major differences are observed for the bridging phosphido ligands containing Tipp moieties, as can be observed in the IR spectrum (Table 3) and in the catalytic activity data (Table 1). Although polycarbonyl CO frequencies are not directly proportional to the strength of the CO bond but may also depend on the geometry of the molecule, in our case the orthogonality among the carbonyls will display their electronic effect through the metal center as corroborated by the NMR data.

Although no metal–metal bond is found in the solid state structures of the early/late transition metal complexes [44], extended Hückel molecular orbital calculations performed on the model complexes [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr( $\mu$ -PH<sub>2</sub>)<sub>2</sub>M'L<sub>n</sub>](M'L<sub>n</sub> = Pt(PH<sub>3</sub>)<sub>2</sub>, Rh( $\eta$ -indenyl), Pt(Me<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>, Mo(CO)<sub>4</sub>) indicate the presence of M'  $\Rightarrow$  Zr donor acceptor bonds that become weaker in the series Pt > Rh > Ni > Mo. Interestingly, our results are in close agreement with the theoretically expected reactivity order Mo > Cr  $\approx$  Ni [47].

## 2.2. Catalytic polymerization of propylene promoted by the monometallic complexes **6–8**

It is interesting to compare the propylene polymerization results of the heterodinuclear complexes **1–5** with the corresponding mononuclear precursor complexes **6** and **7** and the zirconocene monophosphido complex **8** (Table 4). A similar trend is observed for the bisphosphido zirconocene complexes **6** and **7**, with regards to the catalyst/MAO ratio and tempera-

Table 3

CO stretching bands (cm<sup>-1</sup>) for the bridged catalysts

Catalyst	Before MAO addition	After MAO addition
<b>1</b>	1942.8	1874.5
	1995.1	1909.7
	2000.9	2000.4
	2011.4	
<b>2</b>	1954.3	1943.2
	1990.1	1989.7
<b>3</b>	1852.3	1988.5 (broad)
	1865.9	
	1882.0	
	1976.2	
<b>4</b>	1881.7	1859.9
	1897.1	1876.3 (shoulder)
	1991.4	1941.8
<b>5</b>	1883.5	1858.4
	1895.9	1873.5
	1987.4	1940.6

Table 4

Activity data for the polymerization of propylene with complexes **6–8**

Entry	Catalyst	[catal] <sup>a,b</sup> (mmol)	<i>T</i> (°K)	MAO <sup>c</sup> (mmol)	Cat/MAO ratio	Activity <sup>d</sup>
1	<b>6</b>	$8.68 \times 10^{-3}$	303	6.38	1:1000	$1.8 \times 10^5$
2	<b>6</b>	$8.68 \times 10^{-3}$	303	8.62	1:1350	$7.1 \times 10^4$
3	<b>6</b>	$8.68 \times 10^{-3}$	303	17.24	1:2700	$6.2 \times 10^4$
4	<b>6</b>	$8.68 \times 10^{-3}$	333	8.62	1:1350	$4.2 \times 10^4$
5	<b>7</b>	$7.22 \times 10^{-3}$	273	17.24	1:2700	$3.3 \times 10^4$
6	<b>7</b>	$7.22 \times 10^{-3}$	303	6.38	1:1000	$4.2 \times 10^4$
7	<b>7</b>	$7.22 \times 10^{-3}$	303	8.62	1:1350	$5.2 \times 10^4$
8	<b>7</b>	$7.22 \times 10^{-3}$	303	17.24	1:2700	$3.8 \times 10^4$
9	<b>7</b>	$7.22 \times 10^{-3}$	333	8.62	1:1350	$6.2 \times 10^4$
10	<b>8</b>	$7.91 \times 10^{-3}$	273	8.62	1:1350	$1.1 \times 10^5$
11	<b>8</b>	$7.91 \times 10^{-3}$	303	6.38	1:1000	$1.2 \times 10^5$
12	<b>8</b>	$7.91 \times 10^{-3}$	303	8.62	1:1350	$1.7 \times 10^5$
13	<b>8</b>	$7.91 \times 10^{-3}$	303	17.24	1:2700	$2.2 \times 10^5$

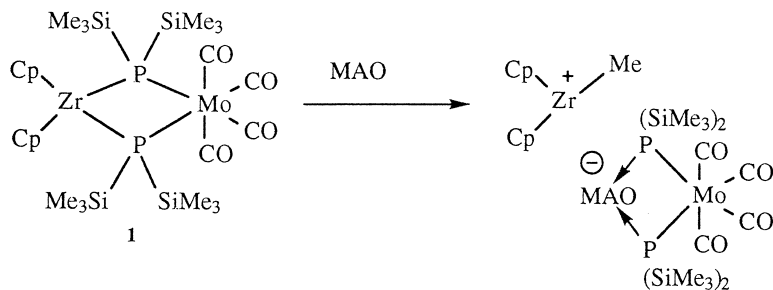
<sup>a</sup>In 30 ml toluene.<sup>b</sup>Atmospheric pressure.<sup>c</sup>Methylalumoxane, solvent removed from a 20 wt% solution in toluene (Witco) at 25°C/10<sup>-6</sup> Torr.<sup>d</sup>Grams total polymer/mol Zr (mol l<sup>-1</sup>) h atm.

ture, as compared with the heterodinuclear complexes or similar bisamido Group IV complexes [39]. For the monochloro phosphido methylcyclopentadienyl zirconium complex **8**, the catalytic polymerization activity towards propylene was found to be the highest as compared to the other mono and bimetallic zirconocene complexes **1–7**. In addition, the catalytic behavior exhibited by complex **8**, with regard to the catalyst/cocatalyst ratio and temperature effects, is similar to that observed for [Cp<sub>2</sub>ZrCl<sub>2</sub>] or other zirconocene complexes.

In all the reactions, the polymer microstructure was characterized in solution by <sup>1</sup>H and <sup>13</sup>C-NMR spectroscopy according to standard protocols [37]. The end group analysis, which provides important insight into the chain transfer processes occurring in the polymerization, shows a vinylidene/*n*-propyl end groups for all

the obtained polymers, suggesting that β-hydrogen elimination is the most important pathway for chain termination.

In the last few years, it has been found that the active catalyst for the polymerization of α-olefins contains a cationic metal–alkyl moiety ([48] and references therein). Rapid additional insertions of the α-olefin monomers into this cationic complex affords the final polymer. In our case, the cationic methyl zirconocene complexes (Eq. (1)) are formed by the metathesis reaction of the MAO cocatalyst, which breaks the weak early transition metal–phosphido bond (64 kcal mol<sup>-1</sup>), as is found similarly for MAO with these heterobinuclear complexes in the polymerization of ethylene [1], for AlMe<sub>3</sub> with [Cp<sub>2</sub>ZrCIP(SiMe<sub>3</sub>)<sub>2</sub>] [43] and for methylalumoxane with bis(amido)-Group-IV metallocene complexes [39].



The reactions of these and other binuclear complexes with other  $\alpha$ -olefins, silanes and characterization of the active species is currently being investigated.

### 3. Experimental

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, ethylene and nitrogen were purified by passage through a  $MnO$  oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents (THF-*d*8) were distilled under argon from sodium benzophenone ketyl. Hydrocarbon solvents (toluene-*d*8, benzene-*d*6) 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 [49]. NMR spectra were recorded on Bruker DRX 400, Bruker AM 200 and Bruker AM 400 spectrometers.  $^1H$ -NMR and  $^{13}C$ -NMR chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. The NMR experiments were conducted in teflon valve-sealed tubes (J. Young) after vacuum transfer of the liquids on a high-vacuum line. The IR spectra were recorded as a KBr mull on a Zeiss Specord M80 in the range 300–4000  $cm^{-1}$  or on a Nicolet 400 FTIR spectrometer with Na/K dried nujol in an air-free container.

Compounds **1** [44], **2** [1], **3** [44], **4** [45], **5** [45], **6** [43], and **8** [46] were prepared according to literature procedures; compound **7** was prepared according to the synthesis of  $Cp'_2Zr(PHTipp)_2$  [46].

#### 3.1. Propylene polymerization experiments

These experiments were conducted in a 100 ml flamed round-bottom reaction flask attached

to a high-vacuum line. In a typical experiment 5 mg ( $6.38 \times 10^{-3}$  mmol) of the precatalyst **1** and 370 mg of MAO (Zr:Al = 1:1000) were charged into the flask containing a magnetic stir bar. The reaction vessel was connected to a high-vacuum line, pumped down and back-filled three times, the flask re-evacuated, and a measured quantity of toluene (30 ml) was vacuum transferred into the reaction flask from Na/K. After temperature equilibration, the gaseous propylene was admitted to the vessel through a gas purification column. The gas pressure was continuously maintained at 1.0 atm with a mercury manometer. Rapid stirring of the solution was initiated and after a measured time interval the polymerization was quenched by injecting a mixture of methanol–HCl. The resulting oil was removed from the vessel, washed three times with toluene and then the combined organic phases were dried over  $MgCl_2$  for several hours. After filtration, the organic solvent was removed under vacuum and the remaining colorless, viscous oil was dried under vacuum.

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