

# $\alpha$ -Zirconium phosphonates as new supports for metallocene catalysts

Stefan Beck<sup>a</sup>, Adrian R. Brough<sup>b</sup>, Manfred Bochmann<sup>a,\*</sup>

<sup>a</sup> Wolfson Materials and Catalysis Centre, School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich NR4 7TJ, UK

<sup>b</sup> Department of Civil Engineering, University of Leeds, CEMU, Leeds LS2 9JT, UK

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## Abstract

Homoleptic and mixed  $\alpha$ -zirconium phosphonates (ZrPs)  $\alpha$ -Zr(O<sub>3</sub>PR)<sub>2</sub> (R = Me, Bu<sup>n</sup>, Bu<sup>i</sup>, Hex, Oct and Ph) and  $\alpha$ -Zr(O<sub>3</sub>PR<sup>1</sup>)<sub>2-x</sub>(O<sub>3</sub>PR<sup>2</sup>)<sub>x</sub> were readily prepared in high yields from zirconyl chloride and the corresponding phosphonic acids in suitable solvent mixtures under hydrothermal conditions at low fluoride concentrations. They form crystalline aggregates consisting of platelets from ca. 10–20 monolayers thickness, with well-defined surface structures. Impregnation with Cp<sub>2</sub>ZrCl<sub>2</sub> by sublimation or slurry methods provided the first examples of ZrP-supported alkene polymerization catalysts. Crystal morphology and interlayer spacing are unaffected by the impregnation process. Solid-state NMR spectroscopy provides evidence for the integrity of the adsorbed metallocene structure. Covalent attachment of Cp\*ZrCl<sub>3</sub> to functionalized ZrPs of the type  $\alpha$ -Zr(O<sub>3</sub>PR<sup>1</sup>)<sub>1.8</sub>(O<sub>3</sub>PC<sub>n</sub>H<sub>2n</sub>OH)<sub>0.2</sub> is similarly possible. The new catalysts polymerize ethene with good to excellent activities under mild conditions, even at remarkably low methylalumoxane/zirconocene ratios of 10:1. The polymer is obtained as free-flowing particles, which reflect the morphology of the catalyst supports.

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## 1. Introduction

Metallocene-based olefin polymerization catalysts are known for their high activity and versatility. However, for most industrial applications catalyst heterogenization is required [1–3]. Most supporting concepts for the heterogenization of metallocene catalysts use different types of amorphous silica [4–8], although MgCl<sub>2</sub> [9–11], alumina [12], zeolites [13,14], clays [15,16], mesoporous silicates [17–21] and polymers [22–28] have also been used. We report here the use of zirconium phosphonates as supports for metallocene catalysts.

Zirconium phosphonates, [ $\alpha$ -Zr(O<sub>3</sub>PR)<sub>2</sub>]<sub>∞</sub> (ZrP's) [29], are a family of compounds with layer structure and are available with a wide variety of substituents R (Fig. 1) [30]. They are thermally and chemically very robust; typically, thermogravimetric studies show no weight loss up to ca. 300 °C (unless there is interlamellar water), while some

more stable examples resist temperatures up to ca. 600 °C [31]. The distance between two Zr atoms within a layer is almost identical in all  $\alpha$ -zirconium phosphonates structures ( $r = 5.3 \text{ \AA}$ ) and therefore an area of ca. 24 Å<sup>2</sup> is available for each phosphonate ligand, so that with suitably bulky groups R the surface may be densely packed with organic residues. It was this feature that attracted us to this class of compounds as catalyst supports: as crystalline compounds they provide a well-defined uniform support surface, and the two-dimensional geometry prevents substrate transport limitations, while the surface coverage of hydrocarbyl substituents can be expected to minimize the interaction of catalytically active species with surface oxides, an aspect that might be expected to be a particular advantage in the case of oxophilic early transition metal catalysts. Previously zirconium phosphonates have for example been investigated as protonic conductors [32], oxidation catalysts [33], ion selective materials [34], for photochemical energy conversion [35], as non-linear optical materials [36] and as an acid catalyst for esterification [37]. With the exception of one report on rhodium carbonylation catalysts attached to phosphine-substituted ZrPs [38], their use as

\* Corresponding author. Tel.: +44-1603-592044; fax: +44-1603-592044.

E-mail address: [m.bochmann@uea.ac.uk](mailto:m.bochmann@uea.ac.uk) (M. Bochmann).

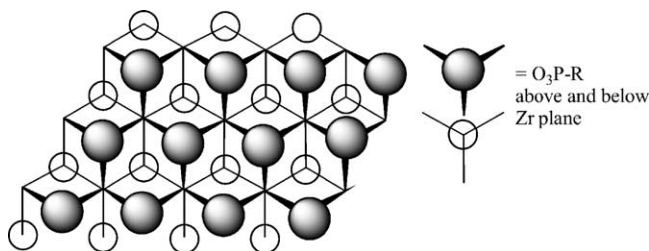
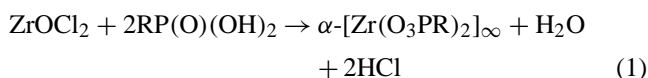


Fig. 1. Schematic view of a zirconium phosphonate layer, showing the octahedral environment of the metal centers and the surface coverage by hydrocarbyl substituents.

tailored catalyst supports has to our knowledge not been explored.

### 1.1. Synthesis

Zirconium phosphonates are prepared from  $\text{ZrOCl}_2$  and phosphonic acids under hydrothermal conditions (Eq. (1)). Earlier studies had reported that the addition of HF was required, preferably at a F/Zr ratio of 6:1, to prevent premature precipitation and to obtain highly crystalline material [29]. We found that this method is not suitable for syntheses involving phosphonic acids with longer alkyl chains which have low solubility in aqueous media, and the high  $\text{F}^-$  content often led to unacceptably low yields of crystalline material. In fact, even material synthesized by precipitation immediately on combining the reagents possessed good crystallinity and gave sharp XRD signals, and high fluoride content was not needed to obtain crystalline material.



Refluxing zirconyl chloride and the phosphonic acid in a water/*n*-propanol solvent mixture not only overcame the solubility problem but allowed the F/Zr ratio to be reduced to 1:1 [39]. These syntheses were conducted in a polypropylene flask equipped with a stainless steel condenser; this method avoided the worrying evaporation of excess HF and the yields were higher than in the experiments with higher fluoride ratios, where HF-induced decomposition of phosphonic acids can occur. The compounds  $\alpha\text{-Zr}(\text{O}_3\text{PMe})_2$  (**1**),  $\alpha\text{-Zr}(\text{O}_3\text{PBu}^n)_2$  (**2**),  $\alpha\text{-Zr}(\text{O}_3\text{PBu}^i)_2$  (**3**),  $\alpha\text{-Zr}(\text{O}_3\text{PHex})_2$  (**4**),  $\alpha\text{-Zr}(\text{O}_3\text{POct})_2$  (**5**) and  $\alpha\text{-Zr}(\text{O}_3\text{PPh})_2$  (**6**) were obtained in 70–95% yield.

Mixed ZrP materials were obtained from a mixture of different phosphonic acids at the appropriate molar ratios. This method was employed for the preparation of  $\alpha\text{-Zr}(\text{O}_3\text{PMe})_{1.7}(\text{O}_3\text{PCH}_2\text{-CMe}_2\text{CH}_2\text{OH})_{0.3}$  (**7H**),  $\alpha\text{-Zr}(\text{O}_3\text{P}^n\text{Bu})_{1.8}(\text{O}_3\text{PCH}_2\text{CMe}_2\text{CH}_2\text{OH})_{0.2}$  (**8H**),  $\alpha\text{-Zr}(\text{O}_3\text{POct})_{1.8}(\text{O}_3\text{P}-(\text{CH}_2)_9\text{OH})_{0.2}$  (**9H**) and  $\alpha\text{-Zr}(\text{O}_3\text{PPh})_{1.8}(\text{O}_3\text{PCH}_2\text{C}_6\text{H}_4\text{OH})_{0.2}$  (**10H**). The zirconium phosphonates obtained by this method are microcrystalline solids characterized by sharp X-ray powder diffraction (XRD) patterns. Scanning

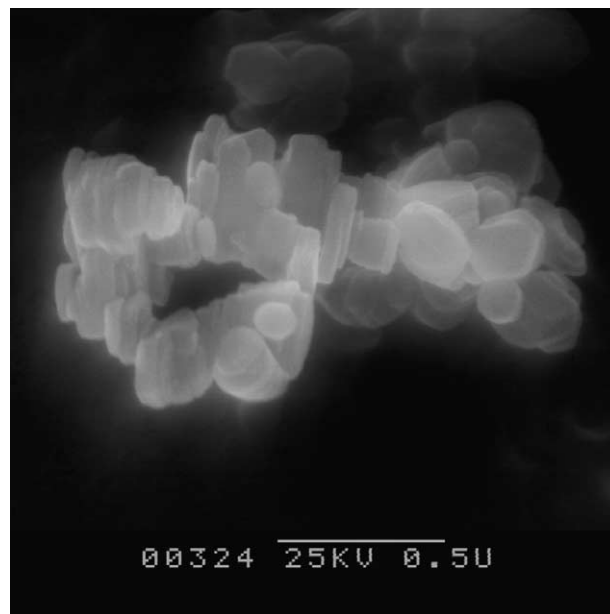


Fig. 2. SEM image of  $\alpha\text{-}[\text{Zr}(\text{O}_3\text{POct})_2]_\infty$ , showing platelet structure. Most platelets are about 10 molecular layers thick. Scale bar represents 0.5  $\mu\text{m}$ .

electron micrographs (SEM) show crystalline platelets. ZrPs with longer alkyl substituents tend to form smaller crystallites than shorter, more hydrophilic phosphonates and give platelets about 10–20 monolayers thick (Fig. 2). These crystallites tend to aggregate to more or less spherical particles with diameters ranging from 1 to 10  $\mu\text{m}$  (Fig. 3).

### 1.2. Catalyst preparation and characterization

For catalyst preparation, two strategies were explored: the impregnation of unsubstituted ZrP materials with zirconocenes, and secondly the covalent attachment of zirconocene derivatives to OH-functionalized zirconium phosphonates.

As a first approach to catalyst preparation, a number of *n*-alkyl or phenyl substituted ZrPs **1–6** were treated with  $\text{Cp}_2\text{ZrX}_2$  ( $\text{X} = \text{Cl}, \text{Me}$ ). Two methods were employed: impregnation by vacuum sublimation, and slurry impregnation in toluene.

For the impregnation of support materials with zirconocenes via sublimation, **1** was mixed thoroughly with 0.3 molar equivalents of  $\text{Cp}_2\text{ZrCl}_2$  and heated to 170  $^\circ\text{C}$ . Similarly, ZrPs were impregnated with the more volatile  $\text{Cp}_2\text{ZrMe}_2$ , in which case heating was carried out at 110  $^\circ\text{C}$ . The excess metallocene was removed by sublimation, leaving materials of composition  $\alpha\text{-Zr}(\text{O}_3\text{PMe})_2(\text{Cp}_2\text{ZrCl}_2)_{0.24}$  (**11**) and  $\alpha\text{-Zr}(\text{O}_3\text{PMe})_2(\text{Cp}_2\text{ZrMe}_2)_{0.01}$  (**12**). The comparison of XRD patterns of the starting material and the supported material showed no relevant changes in the interlayer distances (maximum  $\Delta d = 0.1 \text{ \AA}$ ); suggesting that there was no significant intercalation of the metallocene,

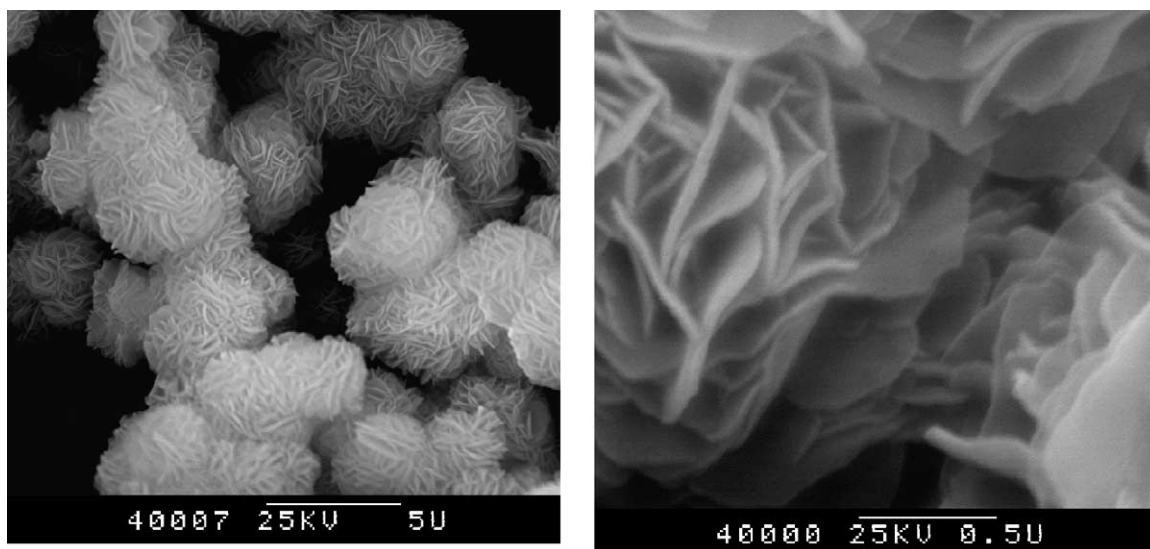


Fig. 3. SEM image of  $\text{Zr}(\text{O}_3\text{PMe})_{1.7}(\text{O}_3\text{PCH}_2\text{CMe}_2\text{CH}_2\text{OH})_{0.3}$ . Left: typical spherical morphology of polycrystallites (scale bar = 5  $\mu\text{m}$ ). Right: Detail of crystallite particle (scale bar = 0.5  $\mu\text{m}$ ).

even if the ZrP/zirconocene mixtures had been heated to 170 °C in sealed tubes for several days. The same result was obtained with ZrPs containing substituents of different chain lengths and wider interlayer spacing, e.g.  $\alpha\text{-Zr}(\text{O}_3\text{PMe})(\text{O}_3\text{POct})$ .

For the impregnation of  $\alpha$ -zirconium phosphonates with zirconocenes by the slurry technique we used the support materials **1–3**, **5** and **6**. Compound **1** was impregnated with  $\text{Cp}_2\text{ZrCl}_2$  as well as  $\text{Cp}_2\text{ZrMe}_2$ ; for the other materials only the dichloride complex was used. Slurries of each zirconium phosphonate solution were stirred for several days with toluene solutions of  $\text{Cp}_2\text{ZrCl}_2$ , in a ZrP/metallocene molar ratio of 3:1. For impregnation with  $\text{Cp}_2\text{ZrMe}_2$  light petroleum was used as the solvent. Any excess zirconocene complex was removed by washing at least four times. XRD measurements of these materials gave similar results to those produced by the sublimation technique, i.e. impregnation did not alter the interlayer spacing. The same results were found when mixtures of ZrPs and zirconocenes in toluene were heated to reflux for several days; again there was no sign of intercalation.

As shown by polymerization studies and solid-state  $^{13}\text{C}$  MAS NMR experiments, the impregnation resulted in low concentrations of metallocenes being attached to the supports, possibly at the edges of crystallites. Within detection limits, MAS NMR proved to be the technique of choice for the quantification of the zirconocene content. For materials with lower metallocene content, long acquisition times were required (e.g. 24 h). The cyclopentadienyl ligands showed a large chemical shift anisotropy, i.e. integration over all spinning sidebands was required. In cases of poor signal/noise ratio, the pattern was reconstructed from the observed high intensity peaks, and the expected pattern as determined from spectra of the pure metallocene.

The catalyst systems prepared by the sublimation method showed higher zirconocene contents in the NMR studies than the zirconium phosphonates prepared by the slurry method; for example, sample **11** showed the composition  $\text{Zr}(\text{O}_3\text{PMe})_2(\text{Cp}_2\text{ZrCl}_2)_{0.24}$ , while **12** has a lower zirconocene content,  $\text{Zr}(\text{O}_3\text{PMe})_2(\text{Cp}_2\text{ZrMe}_2)_{0.01}$ . In the NMR spectra of both materials the sidebands of the cyclopentadienyl ligands are resolved (Fig. 4). The data do not provide information about the mode of metallocene attachment; the presence of spinning sidebands for the supported material does indicate, however, that the metallocene is held rigidly and is not tumbling isotropically in the structure.

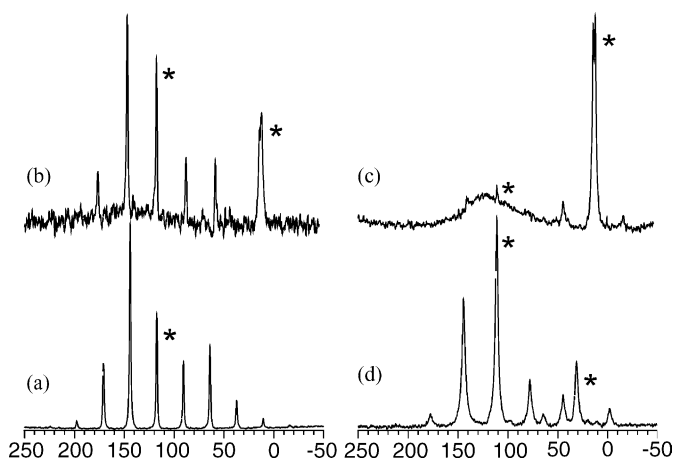


Fig. 4.  $^{13}\text{C}$  MAS NMR spectra of (a) solid  $\text{Cp}_2\text{ZrCl}_2$ ; (b)  $\text{Zr}(\text{O}_3\text{PMe})_2 \cdot (\text{Cp}_2\text{ZrCl}_2)_{0.24}$ ; (c)  $\text{Zr}(\text{O}_3\text{PMe})_2 \cdot (\text{Cp}_2\text{ZrMe}_2)_{0.01}$ ; and (d) solid  $\text{Cp}_2\text{ZrMe}_2$ . The main isotropic peaks are marked by \*, additional peaks are spinning sidebands. The broad signal in the region 150–50 ppm is background signal from the NMR probe.

The  $^{13}\text{C}$  P–Me signal of **1** appears as a doublet separated by ca. 150 Hz, consistent with the  $^{31}\text{P}$ – $^{13}\text{C}$  coupling constant of 135–145 Hz found for phosphonic acids. Interestingly, comparison between the spectra of the supported catalyst and pure methyl zirconium phosphonate showed that the phosphorus–methyl signal of the untreated **1** possesses a fine structure that is lost after metallocene impregnation (Fig. 5). The supported methyl zirconium phosphonates which were produced by the slurry method showed exactly the same loss of fine structure in the signals. This excludes the possibility that the change in signal shape was due to the heating of the material in the sublimation process. ZrP materials containing much lower zirconocene concentrations, e.g.  $\alpha\text{-Zr}(\text{O}_3\text{PMe})_2\cdot(\text{Cp}_2\text{ZrCl}_2)_{0.002}$  prepared by slurry impregnation, show the same effect, while refluxing **1** in neat toluene for extended periods of time did not lead to changes in the signal pattern. The reason for the fine structure of **1** could not be determined unequivocally; however, comparison of  $\alpha\text{-Zr}(\text{O}_3\text{PMe})_2$  samples with different crystallinities showed that the left shoulder at  $\delta$  16.5 is presumably caused by methyl groups located on the edges of microcrystalline particles, since in samples with larger crystals this shoulder is barely detectable.

A similar fine structure could not be seen for the zirconium phosphonates with longer alkyl chains, and spectra of the supported and unsupported materials in this region are essentially identical. The data indicate low zirconocene coverage, giving rise to compositions  $\alpha\text{-}(\mathbf{2})(\text{Cp}_2\text{ZrCl}_2)_{0.002}$  and  $(\mathbf{3})\text{Cp}_2\text{ZrCl}_2)_{0.001}$ . For the catalyst precursors  $(\mathbf{5})(\text{Cp}_2\text{ZrCl}_2)_x$  and  $(\mathbf{6})(\text{Cp}_2\text{ZrCl}_2)_x$  cyclopentadienyl signals could not be detected; given the resolution limits of these spectra, in these cases the metallocene content was taken to be equal to the upper detection limit, i.e.  $x = 0.008$  and  $0.003$  for impregnated **5** and **6**, respectively. These figures were used for calculating the catalyst productivities. Catalyst compositions based on these data are given in Table 1.

For the functionalized zirconium phosphonates  $\alpha\text{-Zr}(\text{O}_3\text{PMe})_{1.7}\text{-(O}_3\text{PCH}_2\text{-CMe}_2\text{CH}_2\text{OH)}_{0.3}$  (**7H**),  $\alpha\text{-Zr}(\text{O}_3\text{P}^n\text{ octyl)}_{1.8}\text{-(O}_3\text{P-(CH}_2)_9\text{OH)}_{0.2}$  (**9H**) and  $\alpha\text{-Zr}(\text{O}_3\text{PPh})_{1.8}\text{(O}_3\text{PCH}_2\text{C}_6\text{H}_4\text{OH)}_{0.2}$  (**10H**) a different mode of catalyst impregnation was employed, the covalent attachment via

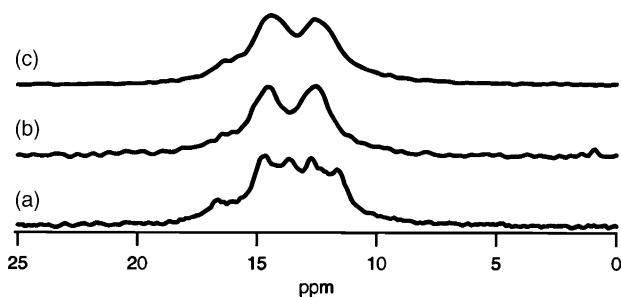


Fig. 5. P–CH<sub>3</sub> region of  $^{13}\text{C}$  MAS-NMR spectra of phosphonate supported catalysts. (a)  $\alpha\text{-Zr}(\text{O}_3\text{PMe})_2$  (**1**); (b)  $\text{Zr}(\text{O}_3\text{PMe})_2(\text{Cp}_2\text{ZrMe}_2)_{0.01}$  (**12**); and (c)  $\text{Zr}(\text{O}_3\text{PMe})_2\cdot(\text{Cp}_2\text{ZrCl}_2)_{0.24}$  (**11**).

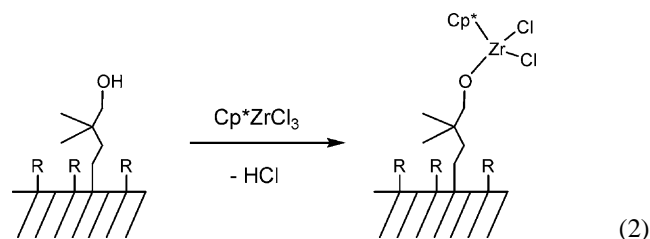
Table 1

Compositions of ZrP-supported zirconocene catalysts

Catalyst	Impregnation process
( <b>11</b> ) $\alpha\text{-Zr}(\text{O}_3\text{PMe})_2\cdot(\text{Cp}_2\text{ZrCl}_2)_{0.24}$	Sublimation
( <b>12</b> ) $\alpha\text{-Zr}(\text{O}_3\text{PMe})_2\cdot(\text{Cp}_2\text{ZrMe}_2)_{0.01}$	Sublimation
( <b>13</b> ) $\alpha\text{-Zr}(\text{O}_3\text{PMe})_2\cdot(\text{Cp}_2\text{ZrCl}_2)_{0.002}$	Slurry
( <b>14</b> ) $\alpha\text{-Zr}(\text{O}_3\text{PMe})_2\cdot(\text{Cp}_2\text{ZrMe}_2)_{0.002}$	Slurry
( <b>15</b> ) $\alpha\text{-Zr}(\text{O}_3\text{Pbu}^n)_2\cdot(\text{Cp}_2\text{ZrCl}_2)_{0.002}$	Slurry
( <b>16</b> ) $\alpha\text{-Zr}(\text{O}_3\text{Pbu}^t)_2\cdot(\text{Cp}_2\text{ZrMe}_2)_{0.001}$	Slurry
( <b>17</b> ) $\alpha\text{-Zr}(\text{O}_3\text{POct})_2\cdot(\text{Cp}_2\text{ZrCl}_2)_{0.008}$	Slurry
( <b>18</b> ) $\alpha\text{-Zr}(\text{O}_3\text{PPh})_2\cdot(\text{Cp}_2\text{ZrCl}_2)_{0.003}$	Slurry

reaction with the surface –OH functions. Since we had ascertained that intercalation did not take place with these reagents, only the concentration of OH functions on the outside surfaces needed to be considered. Treatment of these compounds with an excess of *n*-butyllithium and back-titration suggested that ca. 10–16% of total OH functions could be deprotonated. This value was used to estimate the level of zirconocene attachment.

Stirring **7H**, **9H** or **10H** with a hexane solution of  $\text{Cp}^*\text{ZrCl}_3$  afforded catalytically active materials of the approximate composition  $\text{Zr}(\text{O}_3\text{PR})_{1.7}\text{-(O}_3\text{PCH}_2\text{-CMe}_2\text{CH}_2\text{OH)}_{0.28}\text{(O}_3\text{PCH}_2\text{-CMe}_2\text{CH}_2\text{OZrCl}_2\text{Cp}^*)_{0.02}$  (**19**, R = Me; **20**, R = Bu<sup>n</sup>; **21**, R = Ph) (Eq. (2)). The reaction of  $\text{Cp}^*\text{ZrCl}_3$  with alcohols is quantitative under these conditions, as shown for example by the reaction of  $\text{Cp}^*\text{ZrCl}_3$  with 1-hexanol in hexane which smoothly produces  $\text{Cp}^*\text{ZrCl}_2(\text{OC}_6\text{H}_{13})$ .



### 1.3. Ethene polymerizations

All the ZrP-supported catalysts were tested for ethene polymerization. The systems were activated either using methylalumoxane (MAO) or  $\text{AlBu}_3^i/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (30:1). As a control, these activators were also applied to the zirconium phosphonate support materials themselves which did not show any catalytic activity.

Catalyst **11** was tested with both activator systems and gave closely similar activities and polymer molecular weights (Table 2, runs 1 and 4). It was suspected, however, that the high zirconocene content in this sample was presumably due to the presence of excess  $\text{Cp}_2\text{ZrCl}_2$  that was not attached but had not been adequately removed by the sublimation process and might therefore lead to leaching of the catalyst. This was indeed borne out, as shown by the activity of the supernatant solution (run 2), compared to that of the solid residue (run 3). The molecular weight of the



Table 2  
Ethene polymerizations with Cp<sub>2</sub>ZrCl<sub>2</sub>/ZrP supported catalysts<sup>a</sup>

Entry	Catalyst	n(α-Zr) (10 <sup>-3</sup> mol)	n(Cp <sub>2</sub> ZrX <sub>2</sub> ) (10 <sup>-6</sup> mol)	Cocatalyst	Al/Zr	Yield PE (g)	Prod. <sup>b</sup>	M <sub>w</sub>	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>
1	α-Zr(O <sub>3</sub> PMe) <sub>2</sub> ·(Cp <sub>2</sub> ZrCl <sub>2</sub> ) <sub>0.24</sub> ( <b>11</b> )	0.537	127.8	MAO (80:1)	80	1.8	168	10200	2000	5.1
2	α-Zr(O <sub>3</sub> PMe) <sub>2</sub> ·(Cp <sub>2</sub> ZrCl <sub>2</sub> ) <sub>0.24</sub> ( <b>11</b> )	0.537	Supernatant solution	MAO	–	1.0	94	12500	2650	4.7
3	α-Zr(O <sub>3</sub> PMe) <sub>2</sub> ·(Cp <sub>2</sub> ZrCl <sub>2</sub> ) <sub>0.24</sub> ( <b>11</b> )	0.537	Precipitate of run 2	MAO	–	1.1	103	55000	7600	7.2
4	α-Zr(O <sub>3</sub> PMe) <sub>2</sub> ·(Cp <sub>2</sub> ZrCl <sub>2</sub> ) <sub>0.24</sub> ( <b>11</b> )	0.537	127.8	AlBu <sub>3</sub> <sup>i</sup> /Ph <sub>3</sub> C <sup>+</sup> B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> <sup>-</sup>	3	1.8	169	9700	1040	9.3
5	α-Zr(O <sub>3</sub> PMe) <sub>2</sub> ·(Cp <sub>2</sub> ZrMe <sub>2</sub> ) <sub>0.01</sub> ( <b>12</b> )	0.5	5	AlBu <sub>3</sub> <sup>i</sup> /Ph <sub>3</sub> C <sup>+</sup> B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> <sup>-</sup>	80	0.55	1320	109000	14500	7.5
6	α-Zr(O <sub>3</sub> PMe) <sub>2</sub> ·(Cp <sub>2</sub> ZrCl <sub>2</sub> ) <sub>0.002</sub> ( <b>13</b> )	1.07	Max. 2	AlBu <sub>3</sub> <sup>i</sup> /Ph <sub>3</sub> C <sup>+</sup> B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> <sup>-</sup>	2000	1.6	9,600	161000	47500	3.4
7	α-Zr(O <sub>3</sub> PMe) <sub>2</sub> ·(Cp <sub>2</sub> ZrMe <sub>2</sub> ) <sub>0.002</sub> ( <b>14</b> )	1.0	Max. 2	AlBu <sub>3</sub> <sup>i</sup> /Ph <sub>3</sub> C <sup>+</sup> B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> <sup>-</sup>	2000	0.55	3,300	233000	71400	3.3
8	α-Zr(O <sub>3</sub> P <sup>i</sup> Bu) <sub>2</sub> ·(Cp <sub>2</sub> ZrCl <sub>2</sub> ) <sub>0.002</sub> ( <b>15</b> )	1.0	ca. 2	AlBu <sub>3</sub> <sup>i</sup> /Ph <sub>3</sub> C <sup>+</sup> B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> <sup>-</sup>	2000	0.4	2,400	424000	37400	11.3
9	α-Zr(O <sub>3</sub> P <sup>i</sup> Bu) <sub>2</sub> ·(Cp <sub>2</sub> ZrCl <sub>2</sub> ) <sub>0.001</sub> ( <b>16</b> )	1.0	ca. 1	AlBu <sub>3</sub> <sup>i</sup> /Ph <sub>3</sub> C <sup>+</sup> B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> <sup>-</sup>	4000	0.15	1,800	274000	40600	6.7

<sup>a</sup> Conditions: glass reactor, 50 mL toluene, 40 °C, 1 bar ethene pressure, reaction time 5 min. For runs 4–9, [Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] = 9.8 × 10<sup>-4</sup> mol/L and [AlBu<sub>3</sub><sup>i</sup>] = 8.58 × 10<sup>-3</sup> mol/L.

<sup>b</sup> Productivity in 'kg PE (mol Cp<sub>2</sub>ZrCl<sub>2</sub>)<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>'.

polymer produced by the residue was ca. four times higher than that produced in the supernatant, while the polydispersity was broader. Similar tests for the other catalyst samples showed negligible activity of the supernatant, i.e. absence of catalyst leaching.

Low catalyst loading increased both the nominal productivity and the polymer molecular weights, cf. runs 5–9 produced polymers with  $\bar{M}_w$  up to 400 000, with a much broader molecular weight distribution than would be found in homogeneous phase catalysts. Although the zirconocene concentration derived from the solid-state NMR measurements should be regarded as guide-line figures only, it is evident that the zirconium phosphonate supported catalysts show high productivities (for a heterogenised catalyst) under only 1 bar ethene pressure, of the order of 10<sup>6</sup>–10<sup>7</sup> g PE (mol zirconocene)<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>. The exceptions are catalysts **17** and **18** which produced only minor amounts of polyethene, insufficient for polymer analysis. It is likely that in these cases the zirconocene loading was significantly lower than the upper limits estimated from NMR detection limits.

The polymer particles obtained with ZrP-supported catalysts tend to replicate the shapes of the agglomerated crystallites. Examples are shown in Fig. 6 for catalysts **16** and **17**. The scanning electron micrographs confirms the even distribution of the active species over the crystallite surface and show sheet-like growth of polymer strands from some segments.

Catalysts derived from the covalent attachment of Cp\*ZrCl<sub>3</sub>, compounds **19–21**, were tested at 25 °C using both MAO and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as activators (Tables 3 and 4). Considering that these polymerizations were carried out at 25 °C rather than 40 °C, the productivities with MAO were comparable but not significantly better than those of catalysts **11–18**. However, in several cases tests with the supernatant solution obtained after such a polymerization run showed catalytic activity, i.e. MAO was capable of removing the organometallic species from the support to some extent, although the rates were significantly less than those of the initial supported catalyst. For this reason, and in view of the added complexity of producing and characterizing these functionalized support materials, catalysts **19–21** were not studied in further detail.

An interesting feature of these reactions was the possibility of obtaining significant polymerization activity at rather low MAO/zirconocene ratios. By comparison, homogeneous reactions usually require Al/Zr ratios of ca. 1000:1 and higher, while at ratios of <300:1 polymerization activity tends to be negligible. Varying the MAO concentrations for catalyst **11** (Table 3) already shows a significant activity of ca. 4 × 10<sup>4</sup> g PE (mol Cp<sub>2</sub>ZrCl<sub>2</sub>)<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup> at an Al/Cp<sub>2</sub>ZrCl<sub>2</sub> ratio as low as 10:1. As expected, the productivity increases further with the Al/Zr ratio, with productivity of >10<sup>6</sup> g PE (mol Cp<sub>2</sub>ZrCl<sub>2</sub>)<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup> being reached at 120:1, at a comparatively low polymeriza-

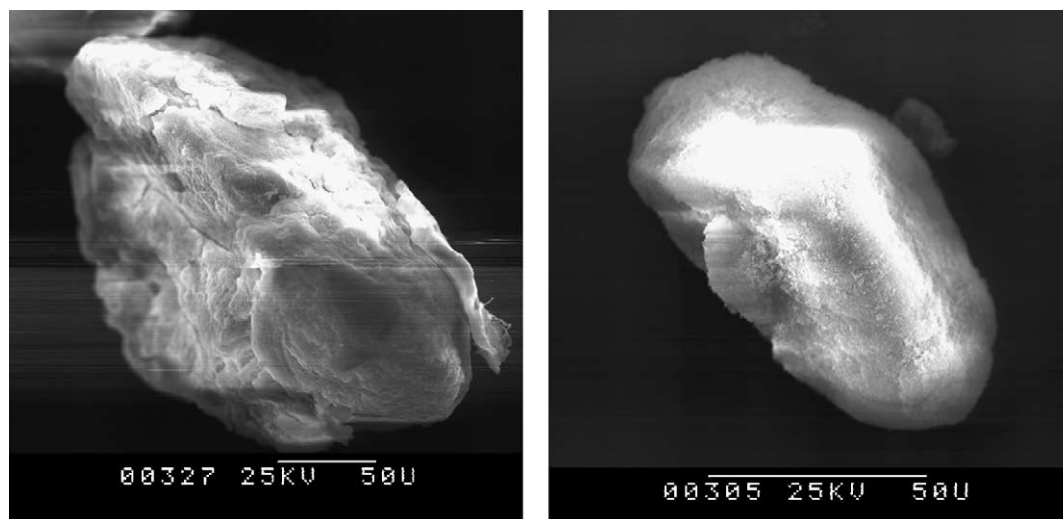


Fig. 6. Polyethylene particle grown on  $Zr(O_3PBu^i)_2(Cp_2ZrCl_2)_{0.001}$  (**16**) (left) and  $Zr(O_3POct)_2(Cp_2ZrCl_2)_{0.008}$  (**17**) (right) (scale bars represent 50  $\mu m$ ). Note the difference in scale compared to the samples shown in Fig. 3.

Table 3

Ethene polymerizations with  $\alpha$ - $Zr(O_3PMe)_2(Cp_2ZrCl_2)_{0.24}$  (**11**) at varying zirconocene/MAO ratios<sup>a</sup>

Run	Catalyst (mg)	$n(\alpha-Zr)$ ( $10^{-6}$ mol)	$n(Cp_2ZrX_2)$ ( $10^{-6}$ mol)	MAO ( $10^{-6}$ mol)	Al/ $Cp_2Zr$ ratio	Yield (g)	Productivity <sup>b</sup>
1	37.0	106.6	25.6	256	10	0.09	42
2	27.9	80.4	19.3	289.5	15	0.17	112
3	26.0	75.0	18.0	360	20	0.16	107
4	27.9	80.4	19.3	386	20	0.14	93
5	18.0	52.0	12.4	496	40	0.82	793
6	23.0	66.0	15.8	1908	120	1.52	1147

<sup>a</sup> Conditions: glass reactor, 50 mL toluene, 40 °C, 1 bar ethene pressure, reaction time 5 min.

<sup>b</sup> Productivity in  $'kg (mol Cp_2ZrCl_2)^{-1} h^{-1} bar^{-1}'$ .

Table 4

Ethene polymerizations with functionalized ZrP catalysts<sup>a</sup>

Run	Catalyst	Activator	$n(\alpha-Zr)$ ( $10^{-3}$ mol)	Active Zr ( $10^{-3}$ mol)	Yield (g)	Prod. <sup>b</sup>	$M_w$	$M_w/M_n$
1	$Zr(O_3PMe)_{1.7}-(O_3PCH_2-CMe_2CH_2OH)_{0.28}-(O_3PCH_2-CMe_2CH_2OZrCl_2Cp^*)_{0.02}$ ( <b>19</b> )	MAO <sup>c</sup>	1	0.02	0.24	48	369000	20.5
2	$Zr(O_3PMe)_{1.7}-(O_3PCH_2-CMe_2CH_2OH)_{0.28}-(O_3PCH_2-CMe_2CH_2OZrCl_2Cp^*)_{0.02}$ ( <b>19</b> )	AlEt <sub>3</sub> /Ph <sub>3</sub> C <sup>+</sup> B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> <sup>-</sup>	1	0.02	0.12	24	220000	53
3	$Zr(O_3POct)_{1.7}-(O_3PCH_2-CMe_2CH_2OH)_{0.28}-(O_3PCH_2-CMe_2CH_2OZrCl_2Cp^*)_{0.02}$ ( <b>20</b> )	MAO <sup>c</sup>	1	0.02	0.62	124	728000	35
4	$Zr(O_3POct)_{1.7}-(O_3PCH_2-CMe_2CH_2OH)_{0.28}-(O_3PCH_2-CMe_2CH_2OZrCl_2Cp^*)_{0.02}$ ( <b>21</b> )	MAO <sup>c</sup>	1	0.02	0.34	68	223000	5

<sup>a</sup> Conditions: glass reactor, 50 mL toluene, 25 °C, 1 bar ethene pressure, reaction time 15 min.

<sup>b</sup> Productivity in  $'kg (mol Cp^*Zr)^{-1} h^{-1} bar^{-1}'$ .

<sup>c</sup> 10 mL MAO solution in toluene, 10 wt.%, Al/Zr ratio 715:1.

tion temperature of 40 °C; the dependence is illustrated in Fig. 7.

## 2. Conclusions

The first application of  $\alpha$ -zirconium phosphonates as convenient and versatile supports for metallocene polymerization catalysts is reported. The materials are suitable for im-

pregnation by both chemisorption and covalent attachment. The most effective method of catalyst attachment proved to be slurry impregnation, which generated catalysts with low metallocene loading. While the metallocene structure is unaffected by attachment, solid-state NMR studies showed that the metallocene is held rigidly and is not tumbling isotropically on the surface.

ZrP-supported zirconocene catalysts are activated at remarkably low Al/metallocene ratios of 10:1, possibly

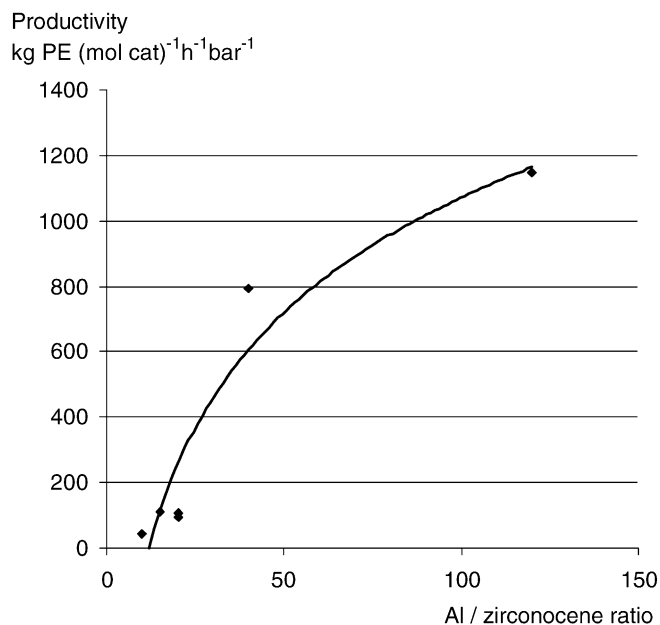


Fig. 7. Dependence of the productivity of catalyst **II** on the MAO/zirconocene ratio.

as the result of the hydrocarbon-like surface structure which is thought to minimize binding of the active metallocene species to surface oxygen atoms. Even a phosphonate–methyl group seems adequate for this purpose. Activities increase with the Al/Zr ratio and reach  $10^6$  g PE (mol  $\text{Cp}_2\text{ZrCl}_2$ )<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup> even under mild conditions (40 °C, 1 bar ethene pressure). Further increases by up to an order of magnitude are observed on activation with  $\text{AlBu}_3^i/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ . Polymers were obtained as free-flowing powders, with particles replicating the morphology of the supported catalysts.

### 3. Experimental

#### 3.1. General

All synthesis and manipulations, except the synthesis of the  $\alpha$ -zirconium phosphonates, were carried out by strict exclusion of moisture and oxygen by use of standard Schlenk techniques or by use of a nitrogen flushed glove-box. All solvents were dried and deoxygenated by standard procedures. The *n*-butyl, *iso*-butyl and *n*-octyl phosphonic acids used for the synthesis of the  $\alpha$ -zirconium phosphonates were synthesized in a slightly modified manner to published methods [31,40].  $(\text{HO})_2\text{P}(\text{O})\text{Me}$ ,  $(\text{HO})_2\text{P}(\text{O})\text{Ph}$ ,  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{C}_6\text{H}_4\text{OMe}$ ,  $\text{Br}(\text{CH}_2)_3\text{CH}_3$ ,  $\text{Br}(\text{CH}_2)_7\text{CH}_3$ ,  $\text{Br}(\text{CH}_2)_9\text{OH}$ , and  $\text{ZrCl}_2\text{O}\cdot 8\text{H}_2\text{O}$  were used as purchased. MAO (10 wt.% toluene solution) was supplied by CK Witco AG.  $\text{AlBu}_3^i$  was supplied by Aldrich.  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  was synthesized by a modified literature procedure [41]. Ethylene 99% was supplied by BOC Gases and dried by

passing through  $\text{P}_4\text{O}_{10}$  and molecular sieve (4 Å) drying columns.

Solution NMR spectra recorded on a Bruker Avance DPX-300 instrument. Solid-state  $^{13}\text{C}$  MAS NMR spectra were obtained at 75.47 MHz using a Bruker MSL-300 spectrometer. Samples were packed into 7 mm zirconia rotors and spun at 2–4.5 kHz. Single pulse spectra were obtained with 45° pulses and with  $^1\text{H}$  decoupling at approximately 40 kHz. Spectra were referenced externally to TMS, using the upfield peak of adamantane ( $\delta$  38.05) as a secondary reference. Typically a 10 s recycle delay was used; this gave some saturation, but relative intensities were not significantly distorted, and the extra scans that could be obtained meant that it was possible to measure the very small signals for the incorporated metallocenes. The changes in chemical shift anisotropy caused by adsorption were generally relatively small (e.g. compare Fig 4a and b) and would not give rise to significant errors when assuming the anisotropy of the bulk solid material to calculate integrals. The metallocene content of  $\text{Cp}_2\text{ZrX}_2/\text{ZrP}$  catalysts at low loading was estimated by  $^{13}\text{C}$  NMR spectroscopy by comparison with simulated spectra at varying ZrP/metallocene ratios, to determine the limit of detection of the most intense metallocene peak.

X-ray powder diffractions were measured on a Philips PW 1700 using a Co radiation source or on a Philips APD1700 XRD diffractometer using a Cu radiation source. The samples were mixed with ca. 10% potassium chloride as an internal reference. The main XRD peak of KCl was calibrated to 3.15 Å. The scanning electron micrograph (SEM) images were recorded using a Hitachi S700 Field Emission scanning electron microscope. Polymer molecular weights were determined using gel permeation chromatography performed by RAPRA Technology Ltd., Shrewsbury.

#### 3.2. Synthesis of acetyl esters

Acetyl chloride (7.8 g, 0.1 mol) was dropped slowly to a toluene solution (200 mL) of 0.1 mol  $\alpha$ -bromo- $\omega$ -hydroxy alkane and 7.9 g pyridine (0.1 mol) at room temperature. A white solid precipitated. The reaction was stirred for 2–3 h and filtered over  $\text{MgSO}_4$ . The solvent was removed in vacuum. The resulting oil was pure by NMR.  $\text{BrCH}_2\text{CMe}_2\text{CH}_2\text{OC}(\text{O})\text{Me}$ , yield 83% (after distillation, 323 K at 3 mmHg);  $\text{Br}(\text{CH}_2)_9\text{OC}(\text{O})\text{Me}$ , yield 55% (after distillation, 405 K at 10 mmHg).

#### 3.3. Synthesis of the acetyl phosphonic esters

Sodium (11.5 g; 0.5 g atom) was melted and dispersed to a thin mirror in a 1 L flask under vacuum. THF (400 mL) and diethyl phosphite (69.05 g, 0.5 mol) were added dropwise. After stirring the mixture at room temperature for 12 h, 0.5 mol of the bromoalkane were added. Stirring was continued for 12 h. The reaction mixture was filtered, washed with dilute HCl, dried over  $\text{MgSO}_4$  and filtered. The

solvent was removed and the clear liquid phosphonic esters  $(\text{EtO})_2\text{P}(\text{O})\text{R}$  purified by distillation.

### 3.4. Synthesis of the OH-functionalized phosphonic acids

The phosphonic esters (0.5 mol) were refluxed for 10–12 h in ca. 500 mL conc. hydrochloric acid. The higher alkylphosphonic acids crystallized on solvent removal; for phosphonic acids containing shorter alkyl chains benzene was added and removed several times. The acids were washed with toluene and light petroleum and finally dried for several days under vacuum. Purity was checked by NMR.

### 3.5. Synthesis of the $(\text{HO})_2\text{P}(\text{O})\text{CH}_2\text{C}_6\text{H}_4\text{OH}$

$(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{C}_6\text{H}_4\text{OMe}$  (0.2 mol) was refluxed with 200 mL aqu. HBr (48%)/ $\text{H}_2\text{O}$  (1:1) for 3 days. The solvent was evaporated, the oily residue repeatedly treated with benzene and dried under vacuum until a slightly yellow solid remained. The product contained traces of the methoxyphenyl phosphonic acid which could not be removed. Yield 73%.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-d}_6$ , 298 K):  $\delta$  9.68 (br, 3H, OH), 7.02 (d, 2H,  $\text{C}_6\text{H}_4$ ), 6.66 (d, 2H,  $\text{C}_6\text{H}_4$ ), 2.82 (d,  $J_{\text{PH}} = 20.7$  Hz, 2H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{DMSO-d}_6$ , 298 K):  $\delta$  156.5 (1- $\text{C}_6\text{H}_4$ ), 131.5 (2C,  $\text{C}_6\text{H}_4$ ), 124.7 (1C, 6- $\text{C}_6\text{H}_4$ ), 115.7 (2C,  $\text{C}_6\text{H}_4$ ), 35.1 ( $\text{CH}_2$ ).

### 3.6. Reaction of $(\text{C}_5\text{Me}_5)\text{ZrCl}_3$ with 1-hexanol

$(\text{C}_5\text{Me}_5)\text{ZrCl}_3$  and 1-hexanol in a 1:1 molar ratio were mixed in an NMR tube in  $\text{CDCl}_3$ . Monitoring the reaction showed the replacement of the  $^1\text{H}$  NMR signal for  $(\text{C}_5\text{Me}_5)\text{ZrCl}_3$  at  $\delta$  2.17 in a clean and fast reaction to  $(\text{C}_5\text{Me}_5)\text{ZrCl}_2\text{O}(\text{CH}_2)_5\text{CH}_3$  as the single product. The data for the starting materials are included here for comparison.  $(\text{C}_5\text{Me}_5)\text{ZrCl}_3$ :  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  2.17 (s, 15H, Me);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  130.9 ( $\text{C}_5$ ), 13.3 (Me). 1-Hexanol:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  3.48 (t, 2H,  $\text{CH}_2\text{OH}$ ), 1.44 (m, 2H,  $\text{CH}_2$ ), 1.20 (m, 6H,  $(\text{CH}_2)_3$ ), 0.79 (t, 3H, Me).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  62.5 ( $\text{CH}_2\text{OH}$ ), 32.8, 31.5, 25.4, 22.6 (all  $\text{CH}_2$ ), 13.9 (Me).  $(\text{C}_5\text{Me}_5)\text{ZrCl}_2\text{O}(\text{CH}_2)_5\text{CH}_3$ :  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  3.9 (br, 2H,  $\text{CH}_2\text{OZr}$ ),  $\delta$  2.10 (s, 15H, Me), 1.74 (br, 2H,  $\text{CH}_2$ ), 1.26 (m, 6H,  $(\text{CH}_2)_3$ ), 0.86 (t, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  129.7 ( $\text{C}_5$ ), 72.2 ( $\text{CH}_2\text{O}$ ), 31.3, 31.1, 25.0, 22.5 (all  $\text{CH}_2$ ), 14.0 ( $\text{CH}_3$ ), 13.2 ( $\text{Cp}^*$ ).

### 3.7. Synthesis of $\alpha$ -zirconium phosphonates

The syntheses were carried out in a 250 mL polypropylene flask.  $\text{ZrCl}_2\text{O}\cdot\text{H}_2\text{O}$  (0.045 mol) was dissolved in 50 mL water containing 2 mL hydrofluoric acid (40% solution). To this was added dropwise the solution of phosphonic acid (0.090 mol). For  $\text{MePO}_3\text{H}$ , 50 mL  $\text{H}_2\text{O}$  was used; for *n*-butyl, *i*-butyl, *n*-hexyl, *n*-octyl and phenyl phospho-

nic acids the solvent was a  $\text{H}_2\text{O}/1$ -propanol mixture (1:1, 100 mL). A white solid precipitated immediately. Another aliquot of aqu. HF (2 mL) was added, the flask was attached to a stainless steel reflux condenser and heated to 90–100 °C for 5–7 days. The fine-crystalline powder was washed several times with water, 2-propanol, acetone and diethyl ether, using a centrifuge, and dried at 110 °C for 24 h.  $\alpha$ - $\text{Zr}(\text{O}_3\text{PMe})_2$  (**1**), yield 80%. Anal. calc. C, 8.60; H, 2.17. Found C, 8.61; H, 2.06%. XRD (0 0 1): 8.54 Å (preparation with HF/Zr = 6:1); 8.86 (preparation with HF/Zr = 1:1).  $^{13}\text{C}$  MAS-NMR (75.5 MHz, 298 K):  $\delta$  16.2, 14.8, 13.8, 12.9, 11.8 (PMe).

$\alpha$ - $\text{Zr}(\text{O}_3\text{P}^i\text{Bu})_2$  (**2**), yield 77%. Anal. calc. C, 26.44; H, 4.99. Found C, 26.70; H, 5.05%. XRD (0 0 1): 14.63 Å.  $^{13}\text{C}$  MAS-NMR (75.5 MHz, 298 K):  $\delta$  24.7 ( $\text{CH}_2$ ), 13.6 (Me).

$\alpha$ - $\text{Zr}(\text{O}_3\text{P}^t\text{Bu})_2$  (**3**), yield 69%. Anal. calc. C, 26.44; H, 4.99. Found C, 26.70; H, 5.00%. XRD (0 0 1): 14.48 Å.  $^{13}\text{C}$  MAS-NMR (75.5 MHz, 298 K):  $\delta$  32.7 ( $\text{CH}_2$ ), 25.8 (Me), 24.1 (CH).

$\alpha$ - $\text{Zr}(\text{O}_3\text{P}^n\text{Hex})_2$  (**4**), yield 87%. Anal. calc. C, 34.36; H, 6.25. Found C, 34.55; H, 6.10%. XRD (0 0 1), 18.99 Å.

$\alpha$ - $\text{Zr}(\text{O}_3\text{POct})_2$  (**5**), yield 95%. Anal. calc. C, 40.41; H, 7.21. Found C, 40.15; H, 7.25%. XRD (0 0 1): 22.74 Å.  $^{13}\text{C}$  MAS-NMR (75.5 MHz, 298 K):  $\delta$  35.1, 33.8, 25.4, 23.0, 15.3.

$\alpha$ - $\text{Zr}(\text{O}_3\text{PPH}_2)_2$  (**6**), yield 85%. Anal. calc. C, 35.73; H, 2.50. Found C, 35.70; H, 2.60%. XRD (0 0 1): 14.82 Å.  $^{13}\text{C}$  MAS-NMR (75.5 MHz, 298 K):  $\delta$  134.1, 131.5, 128.7, 127.1.

### 3.8. Synthesis of mixed $\alpha$ -zirconium phosphonates

#### 3.8.1. Method 1

The synthesis was carried out in a 250 mL polypropylene beaker which was placed inside a stainless steel flask.  $\text{ZrCl}_2\text{O}\cdot\text{H}_2\text{O}$  (0.045 mol) was dissolved in 50 mL  $\text{H}_2\text{O}$  containing 6 mL aqueous HF (40%). A mixture of methyl phosphonic acid (0.081 mol) and 2,2'-dimethyl-3-hydroxypropyl-1-phosphonic acid (0.009 mol) in 50 mL water was added. The stainless steel reactor was charged with water containing 5 g  $\text{CaCl}_2$ , up to the liquid level inside the PP beaker. The flask was connected to a stainless steel reflux condenser and heated to 90–100 °C for 5–7 days. The sand-like product was washed several times with  $\text{H}_2\text{O}$ , 2-propanol, acetone and diethyl ether and finally dried at 110 °C for 24 h. Yield 69%. Elemental analysis suggested the composition close to  $\alpha$ - $\text{Zr}(\text{O}_3\text{PMe})_{1.7}(\text{O}_3\text{PCH}_2\text{CMe}_2\text{CH}_2\text{OH})_{0.3}$  (**7**). Anal. calc. C, 11.45; H, 2.61. Found C, 12.30; H, 2.80%. XRD (1 0 0), 11.37 Å.

### 3.9. Synthesis of $\alpha$ - $\text{Zr}(\text{O}_3\text{PR})_{1.8}(\text{O}_3\text{PR}'\text{OH})_{0.2}$ with longer alkyl chains

#### 3.9.1. Method 2

The synthesis was carried out in a 250 mL polypropylene flask. To a solution of  $\text{ZrCl}_2\text{O}\cdot\text{H}_2\text{O}$  (0.045 mol) in 50 mL



H<sub>2</sub>O containing 2 mL aqu. HF (40%) was added dropwise a mixture of the unfunctionalized alkyl or aryl phosphonic acid (0.081 mol) and the functionalized phosphonic acid (0.009 mol) dissolved in a suitable solvent or solvent mixture (50 mL H<sub>2</sub>O for *n*-butyl/2,2'-dimethyl 3-hydroxypropyl; 50 mL H<sub>2</sub>O/50 mL 1-propanol for phenyl/hydroxybenzyl and *n*-octyl/9-hydroxynonyl phosphonic acid). A white solid precipitated immediately. Another 2 mL of 40% aqu. HF were added, the flask was connected to a stainless steel reflux condenser and heated to 90–100 °C for 5–7 days. The fine crystalline powder was washed several times with water, 2-propanol, acetone and diethyl ether using a centrifuge, and finally dried at 110 °C for 24 h.  $\alpha$ -Zr(O<sub>3</sub>P<sup>*n*</sup>Bu)<sub>1.8</sub>-(O<sub>3</sub>PCH<sub>2</sub>CMe<sub>2</sub>-CH<sub>2</sub>OH)<sub>0.2</sub> (**8**), yield 92%. Anal. calc. C, 26.66; H, 5.02. Found C, 26.34; H, 5.10%. XRD (1 0 0), 15.00 Å.  $\alpha$ -Zr(O<sub>3</sub>POct)<sub>1.8</sub>(O<sub>3</sub>P(CH<sub>2</sub>)<sub>9</sub>OH)<sub>0.2</sub> (**9**), yield 99%. Anal. calc. C, 40.40; H, 7.20. Found C, 40.30; H, 7.15%. XRD (1 0 0), 21.05 Å.  $\alpha$ -Zr(O<sub>3</sub>PPh)<sub>1.8</sub>(O<sub>3</sub>PCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OH)<sub>0.2</sub> (**10**), yield 99%. Anal. calc. C, 35.79; H, 2.56. Found C, 36.00; H, 2.70%. XRD (1 0 0), 14.29 Å.

### 3.10. Impregnation by sublimation of Cp<sub>2</sub>ZrCl<sub>2</sub>

Finely powdered Cp<sub>2</sub>ZrCl<sub>2</sub> (0.4 g, 1.37 mmol) and **1** (1.0 g, 3.58 mmol) were mixed thoroughly in a Schlenk tube and heated under a static vacuum to 160–170 °C for 6 h in such a way that the oil bath level was ca. 4 cm higher than the solid level. The residue was separated carefully from any sublimed zirconocene to give **11**, yield 96%.

### 3.11. Impregnation by sublimation of Cp<sub>2</sub>ZrMe<sub>2</sub>

Cp<sub>2</sub>ZrMe<sub>2</sub> (0.34 g, 1.35 mmol) and **1** (1.0 g, 3.58 mol) were mixed thoroughly in a Schlenk flask and heated under vacuum to 100–110 °C for 4 h to give **12**, yield 95%.

### 3.12. Impregnation with Cp<sub>2</sub>ZrCl<sub>2</sub> in toluene suspension

A sample of the chosen zirconium phosphonate (4 mmol) was suspended in a toluene solution (20 mL) containing Cp<sub>2</sub>ZrCl<sub>2</sub> (0.3 g, 1 mmol) and stirred at room temperature for 4–6 days. The suspension was transferred into a centrifuge vessel, washed five times with 70 mL of toluene and the residue dried in vacuum. The yields were essentially quantitative; small losses being due to the washing process:  $\alpha$ -Zr(O<sub>3</sub>PMe)<sub>2</sub>(Cp<sub>2</sub>ZrCl<sub>2</sub>)<sub>0.002</sub> (**13**),  $\alpha$ -Zr(O<sub>3</sub>P<sup>*n*</sup>Bu)<sub>2</sub>(Cp<sub>2</sub>ZrCl<sub>2</sub>)<sub>0.002</sub> (**15**),  $\alpha$ -Zr(O<sub>3</sub>P<sup>*iso*</sup>Bu)<sub>2</sub>(Cp<sub>2</sub>ZrCl<sub>2</sub>)<sub>0.001</sub> (**16**),  $\alpha$ -Zr(O<sub>3</sub>POct)<sub>2</sub>·(Cp<sub>2</sub>ZrCl<sub>2</sub>)<sub>0.008</sub> (**17**),  $\alpha$ -Zr(O<sub>3</sub>PPh)<sub>2</sub>·Cp<sub>2</sub>ZrMe<sub>2</sub>)<sub>0.003</sub> (**18**).

### 3.13. Impregnation with Cp<sub>2</sub>ZrMe<sub>2</sub> in light petroleum suspension

In a procedure analogous to the one described above,  $\alpha$ -Zr(O<sub>3</sub>PMe)<sub>2</sub> (1.11 g, 4 mmol) was suspended in a

light petroleum (20 mL) containing Cp<sub>2</sub>ZrMe<sub>2</sub> (0.25 g, 1 mmol) and stirred for 5 days at room temperature. The solid was separated by centrifugation, washed with 4 × 70 mL light petroleum and dried under vacuum to give  $\alpha$ -Zr(O<sub>3</sub>PMe)<sub>2</sub>(Cp<sub>2</sub>ZrMe<sub>2</sub>)<sub>0.002</sub> (**14**).

### 3.14. Reaction of $\alpha$ -Zr(O<sub>3</sub>PR)<sub>1.8</sub>(O<sub>3</sub>PR'OH)<sub>0.2</sub> with C<sub>5</sub>Me<sub>5</sub>ZrCl<sub>3</sub>

Mixed zirconium phosphonates (3 mmol) and C<sub>5</sub>Me<sub>5</sub>ZrCl<sub>3</sub> (0.3 g, 0.9 mmol) were stirred in ca. 20 mL CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 3 days, washed with 3 × 20 mL CH<sub>2</sub>Cl<sub>2</sub> by use of a centrifuge and dried under vacuum.  $\alpha$ -Zr(O<sub>3</sub>PMe)<sub>1.7</sub>(O<sub>3</sub>PCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>OH)<sub>0.28</sub>-(O<sub>3</sub>PCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O-ZrCl<sub>2</sub>Cp\*)<sub>0.02</sub>. Anal. calc. C, 12.76; H, 2.90. Found C, 12.60; H, 2.70.  $\alpha$ -Zr(O<sub>3</sub>PPh)<sub>1.7</sub>(O<sub>3</sub>PCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>OH)<sub>0.28</sub>-(O<sub>3</sub>PCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O-ZrCl<sub>2</sub>Cp\*)<sub>0.02</sub>, yield 99%. Anal. calc. C, 36.39; H, 2.84; Cl, 3.03. Found C, 35.70; H, 2.63; Cl, 2.59%.

### 3.15. Ethene polymerizations

Polymerizations were conducted in a glass reactor containing 50 mL toluene at 40 °C under 1 bar ethene pressure. For MAO activated polymerizations, a solution of MAO in toluene (7 mL, 10 wt.% MAO) was added to a slurry of the catalyst and stirred for 15 min before being injected into the ethene-saturated toluene solution in the reaction vessel. Polymerizations were stopped after 5 min by injecting ca. 5 mL of methanol. The polymers were precipitated with acidified methanol, filtered and dried at 70 °C for 24 h.

For borate activated systems, the catalyst powder was placed in the reactor and a toluene solution (50 mL) containing AlBu<sub>3</sub><sup>*t*</sup> (0.4 mmol, 0.1 mL) was added. The reaction was started by adding 5 mL of a toluene solution containing 1.29 × 10<sup>-5</sup> mol (12 mg) [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].

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