

Phosphorus-bridged metallocenes: New homogeneous catalysts for the polymerization of propene

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Abstract

The synthesis of a new class of metallocenes for the syndiospecific, aspecific and isospecific polymerization of propene is reported. This has been achieved by the incorporation of a phosphorus linking the cyclopentadienyl-type rings. The catalyst precursors, syndiospecific $\text{PhP}(\text{fluorenyl}-\text{Cp})\text{ZrCl}_2$ (**2**), aspecific $\text{PhP}(\text{fluorenyl})_2\text{ZrCl}_2$ (**4**), and isospecific $\text{PhP}(\text{indenyl})_2\text{ZrCl}_2$ (**5**), $\text{RP}(2\text{-Me},4\text{-Ph-indenyl})_2\text{ZrCl}_2$ ($\text{R} = \text{Ph}$ (**6**); $\text{R} = \text{Pr}$ (**7**)) were prepared. Compound **2**, after activation by methylaluminoxane (MAO), in LIPP at 67°C affords syndiotactic polypropene (s-PP) with an activity of 155 kg s-PP/g Zr · h. The physical properties of the s-PP (stereoregularity and molecular weight) are similar to that of conventional carbon-bridged systems. Ab initio calculations on model compounds assisted in rationalizing the high syndiospecificity of **2** in contrast to the much poorer stereoregularity of closely related $\text{Me}_2\text{Si}(\text{fluorenyl}-\text{Cp})\text{ZrCl}_2$. Aspecific metallocene **4**, after activation with MAO, affords high molecular weight atactic-PP, albeit with a low activity. Metallocenes **6** and **7**, activated by MAO, afford isotactic polypropene (i-PP) with extremely high stereoregularity (> 98% mmmm pentads), melting points 156–160°C and molecular weights tunable in the range 250,000–1,100,000. Activities of up to 580 kg i-PP/g Zr · h for **6**/MAO (LIPP, 67°C, 37 000 equiv. MAO) and 1265 kg i-PP/g Zr · h for **7**/MAO (LIPP, 50°C, 37 000 equiv. MAO) have been obtained. © 1998 Elsevier Science B.V.

1. Introduction

Most major polyolefin manufacturers have devoted considerable R and D effort to the polymerization of olefins by metallocenes [1]. This is because of the ability of metallocenes to produce narrow molecular weight distribution polymers, with controllable stereoregularity and

molecular weight. Non-bridged aspecific systems are highly active for the polymerization of ethylene, or copolymerization of ethylene with other α -olefins, and allows the preparation of LLDPE, elastomers² [2,3], plastomers [2,3] and syndiotactic polystyrene [4–6]. By application of an appropriate bridged ligand environment enables the molecular architecture of the resultant polyolefin to be tuned. For example, bridged metallocenes, activated by a cocatalyst, often

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² Much recent patent literature from Dow and Exxon documents (cyclopentadienyl-amido) MCl_2 ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$)/MAO catalysts for olefin (co)polymerization to elastomers and plastomers.

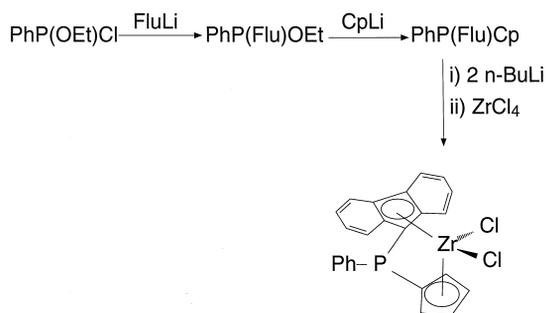


Fig. 1. Preparation of PhP(Flu–Cp)ZrCl₂ (2).

methylaluminoxane (MAO), are highly active for the stereospecific polymerization of propene [7–16] yielding highly isotactic [17,18] and syndiotactic [19] polypropylene (PP). These polypropylenes contain no pure atactic material, and virtually no oligomers.

Ligand modifications to these metallocenes, with retention of the Cp₂ framework, has resulted in polymers with new stereostructures including hemiisotactic [20–22], and stereoblock PP [23,24]. These investigations on metallocene-produced stereoregular polymers have primarily focused on metallocene catalysts which contain certain, similar, structural units. For example, syndiospecific polymerization catalysts contain a carbon-bridged fluorenyl–cyclopentadienyl framework RR'C(fluorenyl–cyclopentadienyl)ZrCl₂ which affords C_s symmetry. Isospecific catalysts normally possess C₂ symmetry and are generally ³ [33] of the type *rac*-Me₂Si(indenyl)₂ZrCl₂ [7–18].

We report here the synthesis and polymerization activity of new syndiospecific, aspecific and isospecific phosphorus-bridged metallocenes. The phosphorus functional group offers a potential route to anchoring of the metallocene to a support. The reactions can be readily moni-

tored by ³¹P NMR spectroscopy. Furthermore, the alkyl substituent on the phosphorus can be extensively varied utilizing readily available RPhCl₂. We had previously discovered that the ethylene polymerization activity of a sulphur-bridged bis(alkoxide) titanium species was an order of magnitude greater than that of its CH₂-bridged analogue [34]. We postulated that this increase in activity could be due to donation of the sulphur lone pair to the titanium ⁴, and wished to investigate whether such an effect might also be present in phosphorus-bridged metallocenes.

2. Results and discussion

2.1. Synthesis and polymerization results of syndiospecific catalysts

The new phosphorus-containing ligand PhP(Flu–Cp) was prepared by sequential addition of fluorenyllithium (1 equiv.), then CpLi (1 equiv.), to PhP(OEt)Cl ⁵ [35]. To inhibit possible double alkylation reactions, the sterically more demanding FluLi was used in the first alkylation step. After conversion of PhP(Flu–Cp) with *n*-BuLi to the dianion Li₂[PhP(Flu–Cp)], reaction with ZrCl₄ in CH₂Cl₂ at –80°C cleanly gave PhP(Flu–Cp)ZrCl₂ (2) as an orange crystalline solid (Fig. 1).

Compound 2 was fully characterized by ¹H, ³¹P and ¹³C NMR and elemental analysis. All resonances were assigned using ¹H–¹H COSY and ¹³C–¹H HETCOR (see Section 4). The ³¹P

³ Other (often C₁ symmetry) systems can also give i-PP. See Refs. [25,26]. Me₂C(Flu)(3-^tBuC₅H₄)ZrCl₂: [27]. See also Refs. [28,29]. Me₂C(3-R-indenyl)(3-^tBuC₅H₃)ZrCl₂ (R = Me, ^tBu): [30]. Me₂Si(2-Me,4-^tBuC₅H₃)₂ZrCl₂: [31,32].

⁴ Okuda et al. [34] demonstrated by X-ray diffraction that the sulphur was indeed coordinated to titanium.

⁵ Sequential reaction of PhPCl₂ with FluLi (1 equiv.), then CpLi (1 equiv.) did not afford PhP(Flu–Cp), but a mixture of products. Reaction of PhPCl₂ with one equiv. of FluLi gave conproportionation with PhPFlu₂, and unreacted PhPCl₂, being the only products.

Table 1

Syndiospecific polymerization of propene using X(Flu–Cp)ZrCl₂ (X = Me₂C, **1**; PhP, **2**; Me₂Si, **3**)/MAO

Catalyst	X	T _{pol} (°C)	Activity (kg/g Zr · h)	LVN (dl/g)	M _w ^a (×10 ⁵)	M _n ^a (×10 ⁵)	m.p. ^b (°C)	rrrr ^c (mol%)
1	C	67	400	1.2	1.2	0.6	134	85
2	P	50	100	2.47	3.0	1.37	128	81
2	P	67	155	1.43	1.3	0.77	119	n.d.
3	Si	67	18	1.27	n.d.	n.d.	n.d.	51

All polymerizations in 1 litre LIPP using 1 μmol of Zr compound, MAO:Zr ratio 1000:1; 5 min prepolymerization at 25°C, polymerization 1 h at stated temperature.

n.d. = not determined ^afrom GPC; ^bfrom DSC; ^cfrom ¹³C NMR.

NMR shift of **2** at δ –37 ppm indicates that the phosphorus is not coordinated to Zr. If coordinated, a ³¹P NMR chemical shift in the region δ 0–20 ppm would be expected.

Polymerization of propene by **2**/MAO in liquid propene (LIPP) gave s-PP at rates of 100 kg s-PP/g Zr · h at 50°C, and 155 kg s-PP/g Zr · h at 67°C. The s-PP has a high syndiotacticity, with 81% rrrr pentads ⁶ Table 1. The stereoregularity and type of stereodeflects are the same, and of a similar intensity, to those in s-PP prepared from Me₂C(Flu–Cp)ZrCl₂ (**1**)/MAO. The disruption of the formal C_s symmetry of PhP(Flu–Cp)ZrCl₂ by the tetrahedral PhP bridge (a lone pair is also present on phosphorus) apparently does not affect the syndiospecificity of the polymerization, the local symmetry at the metal centre not being affected by this remote perturbation ⁷. The s-PP melts at 128°C. This is approximately 5°C less than the melting point of the s-PP obtained from PhMeC(Flu–Cp)ZrCl₂/MAO under similar polymerization conditions [19].

Almost all other s-PP catalysts have the general structural element RR'C(Flu–Cp)ZrCl₂ [19]. In order to study the influence of varying the bridging atom silicon-bridged Me₂Si(Flu–

Cp)ZrCl₂ (**3**)⁸ was made. With MAO as cocatalyst, compound **3** afforded s-PP as a viscous fluid instead of a white powder. Furthermore, the activity was low (see Table 1). The syndiospecificity was only moderate with 51 mol% rrrr pentads ⁹. There were 0.2 mol% 2,1 regiodefects. Two other similar silicon-bridged catalysts are known: Me₂Si(C₅Me₄)(C₅H₄)ZrCl₂ [20] and Me₂Si(phenantraceny)(C₅H₄)ZrCl₂ [20]. After activation with MAO, they afford s-PP (LIPP, 60°C) of low molecular weight and poor stereoregularity, with 24 mol% and 14 mol% rrrr pentads, respectively [20].

The polymer obtained from silicon-bridged **3** has a molecular weight similar to that obtained from carbon-bridged **1**, however, its stereoregularity is clearly much lower than from compounds with a carbon (**1**) or phosphorus (**2**) in the bridge. We have used ab initio calculations to help elucidate the differences in the polymerization characteristics of compounds **1–3**, and the effect on the s-PP produced. This is discussed below.

⁸ The synthesis of **3** has previously been described [37]. It was reported that **3**/MAO (toluene, 50°C) gave a-PP with triads mm = 35 mr = 52 and rr = 13 mol%.

⁹ In our hands, we found that **3**/MAO (LIPP, 67°C) gave a polymer with pentad distribution of mmmm (1.2), mmmr (1.9), rmmr (3.0), mrrm (0.6), mmrr (7.4), rrrm (5.9), rrrr (12.7), mrrm (4.0), mrrr (12.0), rrrr (51.3). The propensity for C_s symmetric metallocenes to give reduced syndiotacticity with lower [propene] has been reported [38].

⁶ Pentad distribution is: mmmm (0.7), mmmr (0.5), rmmr (2.1), mrrm (0.0), mmrr (4.6), rrrm (1.2), rrrr (3.1), mrrm (0.7), mrrr (6.4), rrrr (80.7).

⁷ Syndiospecific propylene polymerization by asymmetric ⁱPrCH(Flu)CpZrCl₂/MAO also gave syndiotactic PP [36].

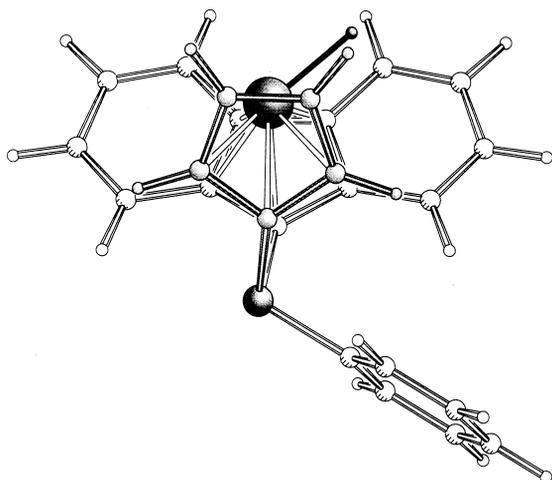


Fig. 2. Calculated (ab initio) structure of $[\text{PhP}(\text{Flu}-\text{Cp})\text{ZrH}]^+$.

2.2. Theoretical analysis

The calculated (ab initio) structure of $[\text{PhP}(\text{Flu}-\text{Cp})\text{ZrH}]^+$ is shown in Fig. 2 below¹⁰.

The difference in polymerization behavior of compounds **1–3** might be related to the steric constraints imposed by the Flu–X–Cp (X = CMe₂, PPh, SiMe₂) wedge. In syndiospecific polymerization, inversion at the metal centre causes a stereoerror. Theoretical studies indicate that such inversion becomes more difficult if the ligand ‘bite angle’ becomes smaller [42]. The structures of a series of model compounds $[\text{X}(\text{Flu}-\text{Cp})\text{ZrH}]^+$ (X = CH₂, SiH₂, PH and PPh) have been calculated to establish whether these variations in the bridging group X affect the geometry of the metallocene significantly. The results of these calculations are collated in Table 2; Fig. 3 illustrates the meaning of the geometric parameters. The CH₂-bridged com-

plex is the most constricted, primarily because the C–X bonds are the shortest. The CXC angle (99.3°) is smaller than tetrahedral, indicating the presence of considerable strain. The SiH₂-bridged system shows a smaller CXC angle (94.3°) because the CSiC bending mode is softer than the CCC bending mode (for a discussion of ligand deformation in *ansa*-metallocenes, see, e.g., Ref. [43]). Nevertheless, the resulting distance (d_{CC}) is larger because of the longer C–X (X=Si) bonds (1.87 Å). The phosphorus-bridged systems (X=PH and PPh) have C–X bonds (1.86 Å) similar to the Si-bridged system, but the CXC angles are more acute (87.8°) because of the preferred CXC angle at phosphorus is close to 90°, i.e., it is much smaller than tetrahedral. Thus, the resulting C–C distances are significantly smaller than for the SiH₂-bridged systems, although still larger than for the CH₂-bridged systems. It therefore seems possible that the observed variations in syndiospecificity for this series of ligands are indeed related to structural changes in the ligand backbone.

2.3. Aspecific catalysts

Ziegler–Natta catalysts produce i-PP together with small amounts (2–5%) of low molecular weight fractions. Although these fractions are often colloquially described as being a-PP, they are not. Atactic-PP is a completely amorphous polymer that has a low T_g and does not crystal-

Table 2
Calculated geometric parameters of $[\text{X}(\text{Flu}-\text{Cp})\text{ZrH}]^+$ systems

X	d_{CX} ^a (Å)	$\angle \text{CXC}$ (°)	d_{CC} ^b (Å)	$\angle \text{Cent-Zr-Cent}$ ^c (°)
CH ₂	1.54	99.3	2.34	121.5
SiH ₂	1.87	94.3	2.73	129.4
PH	1.86	87.7	2.56	127.2
PPh	1.86	87.8	2.57	127.4

^aAverage distance from bridge atom X to fluorenyl or cyclopentadienyl ring.

^bDistance between fluorenyl and cyclopentadienyl rings measured from the carbons adjacent to bridge atom X.

^cAngle extended at Zr between centroids of fluorenyl and cyclopentadienyl rings.

¹⁰ All calculations were of the all-electron closed-shell or open-shell Restricted Hartree–Fock type [39], and were carried out using the GAMESS program [40,41] on IBM RS/6000 and Silicon Graphics Crimson workstations. In the geometry optimizations, the Cp and the fluorenyl groups were constrained to be planar and left/right symmetric, and the phenyl ring was assumed to have an idealized local D_{6h} geometry. Bending was allowed at the Cp–P and Flu–P junctions, and the position of the metal relative to the ligands was not constrained.

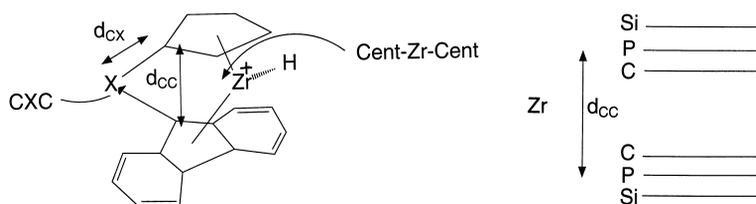


Fig. 3. Representation of $[X(\text{Flu-Cp})\text{ZrH}]^+$ ($X = \text{CH}_2, \text{SiH}_2, \text{HP}, \text{PhP}$) geometries.

lize. Because of the effects of both enantiomeric-site control and chain-end control, preparation of a-PP with metallocene catalysts is not simple¹¹. Metallocene catalysts capable of giving high molecular weight atactic-PP are unusual, examples of which having only recently been disclosed [44,45].

To explore the effect of symmetry on these ‘phosphorus-in-the-bridge’ catalysts, $\text{PhP}(\text{Flu})_2\text{ZrCl}_2$ (**4**) was prepared by conventional synthetic methodology beginning from fluorenyllithium and PhPCl_2 . With MAO as cocatalyst, **4** affords a-PP of a similar high molecular weight (LVN = 1.8 dl/g, $M_v = 190\,000$)¹² and triad distribution (Table 3) as $\text{Me}_2\text{Si}(\text{Flu})_2\text{ZrCl}_2$ [44,45], although the activity is much lower.

2.4. Isospecific catalysts

Isospecific metallocene catalysts based on the bridged bis(indenyl) framework [17,18] necessarily possess C_2 symmetry. Given that the

phosphorus bridge in the syndiospecific **2** did not interfere with the stereoregularity of olefin polymerization, we rationalized that incorporation of a PhP bridge in a bis(indenyl) framework should also allow isospecific polymerization. This synthetic methodology was therefore extended to prepare isospecific $\text{PhP}(\text{indenyl})_2\text{ZrCl}_2$ (**5**), $\text{RP}(2\text{-Me},4\text{-Ph-indenyl})_2\text{ZrCl}_2$ ($R = \text{Ph}$ (**6**); $R = ^i\text{Pr}$ (**7**)) (Fig. 4).

After reaction of $\text{PhP}(\text{indenyl})_2$ with *n*-BuLi to give $\text{Li}_2[\text{PhP}(\text{indenyl})_2]$, reaction of this dianion with ZrCl_4 in CH_2Cl_2 at -80°C afforded **5**. A ca. 1:1 ratio of *rac* and *meso* isomers of **5** were formed. These were separated by fractional crystallization from toluene/ether.

At 67°C , **5**/MAO polymerizes propene to low molecular weight (LVN = 0.33 dl/g), low melting point (117°C), weakly isotactic PP (63 mol% mmmm pentads)¹³ with an activity of 24 kg/g Zr · h. The low melting point is commensurate with the low molecular weight and isotacticity. This is similar to the polymer obtained from the ethylene- or Me_2Si -bridged *rac*-bridge(indenyl)₂ZrCl₂/MAO system [17,18]. M_n is ca. 11 000 as determined by end group analysis in the ¹³C NMR spectrum. There are 1.0 mol% 2,1-regiodefects (*erythro:threo* ratio ca. 1:1) (Fig. 5). The end groups are, as expected, *n*-propyl and vinylidene ($\text{H}_2\text{C}=\text{CMeR}$) in a ca. 1:1 ratio. These arise via conventional propagation/termination pathways of 1,2

¹¹ Achiral catalysts can give rise to some stereospecificity due to error propagation and give stereosequences ...rrrrrrrrrr... where a single meso dyad is the predominant chain error. For example, $\text{Cp}_2\text{MCl}_2/\text{MAO}$ ($M = \text{Zr}, \text{Hf}$) and Cp_2TiPh_2 show a slight preference towards isotacticity. Conversely, $\text{Cp}_2^+\text{MCl}_2/\text{MAO}$ ($M = \text{Zr}, \text{Hf}$) shows a slight tendency to syndiotacticity. At low temperatures ($\ll 0^\circ\text{C}$), chain-end control is the predominant determinant of stereoregularity for such achiral catalysts (see Ref. [9]).

¹² The molecular weight M_v was determined from the LVN by the Mark–Houwink relationship $[\eta] = 9.3 \times 10^{-5} M_v^{0.8}$. This is the empirically derived formula for linear i-PP, and an Mark–Houwink exponent other than 0.8 might be expected for a-PP or s-PP. However, for consistency, we have used the same formula.

¹³ Pentad distribution: mmmm (63.0), mmmr (9.0), rmmr (1.5), mmrr (9.3), mrrm + rrrr (5.2), rrrm (2.3), mrrm (4.1), mrrr (3.5), rrrr (2.0).

Table 3

Polymerization of propene to give atactic-PP

Catalyst	T_{pol} (°C)	Activity (kg/g Zr · h)	LVN (dl/g)	mm (mol%)	mr (mol%)	rr (mol %)
PhP(Flu) ₂ ZrCl ₂ (4)	50	8	1.8	15.7	49.5	34.8
Me ₂ Si(Flu) ₂ ZrCl ₂	50	176	2.2	19	49	32

Polymerizations in 1 litre LIPP. MAO:Zr ratio 1000:1.

propene insertion in a Zr–H bond, followed by termination by β -H transfer to monomer [46].

A class of metallocenes Me₂Si(2-R',4-R''-indenyl)₂ZrCl₂ [17,18] containing judiciously-substituted bridged-indenyl ligands have been developed. After activation with excess MAO, they afford highly isotactic, highly crystalline, high molecular weight polypropene [17,18].

The phosphorus-bridged zirconocene PhP(2-Me,4-Ph-indenyl)₂ZrCl₂ (**6**) was prepared using the same synthetic methodology as **5**. It was not possible to separate the *rac*/*meso* isomers of **6**

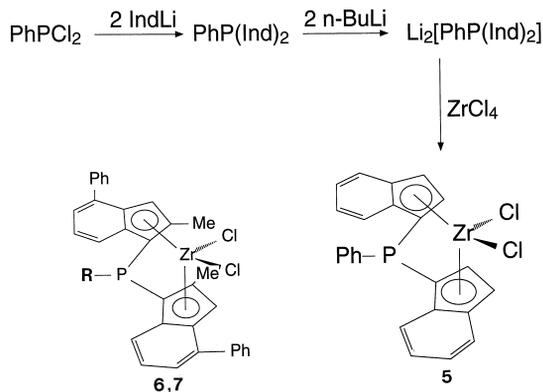
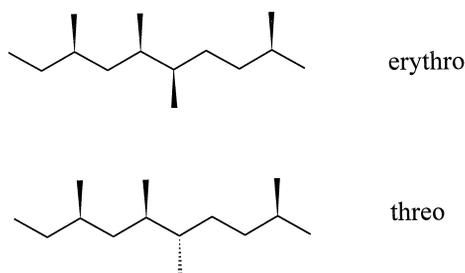


Fig. 4. Synthesis of isospecific polymerization catalysts.

Fig. 5. Representation of *erythro* and *threo* 2,1-regioinsertions.

(ca. 1:2 ratio by ¹H NMR spectroscopy)¹⁴ by repeated crystallization from CH₂Cl₂, and so this mixture was used directly in the polymerization. **6**/MAO afforded highly isotactic polypropene (mmmm = 97.5–98.0% for all entries in Table 4)¹⁵, as well as 4–10% a-PP. In all polymerizations performed with **6**/MAO, there are typically 99.2–99.8 mol% 1,2 insertions, 0.2–0.5 mol% 2,1 regiodefects, and 0.03–0.1 mol% 1,3 regiodefects. The percentage of 2,1 regiodefects does not vary significantly on changing the temperature or Zr:Al ratio. The 2,1-insertion regiodefects are all in the *erythro* form. The melting points were 156–160°C and molecular weights (M_v) were in the range 250 000–1 100 000. According to ¹³C NMR analysis the end groups are primarily isobutyl, indicating that the major chain termination pathway is chain transfer to MAO.

As expected, the melting point of i-PP is not lowered by the presence of amorphous a-PP (*vide supra*). The a-PP is attributed to the 1:2 *rac*:*meso* metallocene isomer ratio (see Section 4). It has been shown that, in general, the *rac*-isomer is much more (10–20 fold) active than the corresponding *meso* isomer for Me₂Si-bridged metallocenes [47]. By ¹³C NMR,

¹⁴ Three methyl resonances of approximately equal intensity are observed in the ¹H NMR. The *rac*-isomer gives rise to one resonance. In the *meso*-isomer the bridging phosphorus is chiral and thus gives rise to two signals for the indenyl 2-methyl groups. Three methyl resonances of equal intensity therefore implies a 1:2 mixture of *rac*:*meso* isomers. In the ³¹P NMR spectrum, three signals are seen for **6** and **7** in a ca. 1:4:1 ratio. This is attributed to the two racemic diastereoisomers (*R* and *S*). The stronger resonance is from the *meso*-diastereoisomer.

¹⁵ Typical pentad distribution was mmmm (98.1), mmmr (0.0), rmmr (0.22), mmrr (0.42), mmrm + rmmr (0.5), rmmr (0.14), mrrm (0.4), mrrr (0.1), rrrr (0.1).

Table 4

Isospecific polymerization of propene using *rac*/*meso*-PhP(2-Me,4-Ph-indenyl)₂ZrCl₂ (**6**)/MAO

Entry	Amt Zr (μmol)	Al/Zr (total)	T _{pol} (°C)	Activity (kg/g Zr · h)	LVN (dl/g)	M _v ^c (×10 ⁵)	m.p. ^d (°C)	a-PP (mol%)
1	1	37 000	50	200 ^b	5.34	8.12	157	4.8
2	1	37 000	67	576 ^b	4.39	6.35	156	4.6
3	1	37 000	67	528 ^b	4.38	6.33	n.d.	4.6
4	4	1 000	67	111 ^a	3.26	4.38	n.d.	10.5
5	8	1 000	67	180 ^a	5.19	7.83	156	9.7
6	4	8 000	50	184 ^b	6.67	10.7	159	2.7
7	4	8 000	50	321 ^{b,c}	2.67	3.41	160	9.0

n.d. = not determined.

All polymerizations in 5 litres LIPP; polymerization 1 h at stated temperature ^a5 min prepolymerization at 23°C; ^b1 min pre-polymerization at 30°C; ^cM_v was determined from the LVN by the Mark–Houwink relationship [η] = 9.3 × 10⁻⁵M_v^{0.8}; ^dfrom DSC; ^e2 vol/vol% H₂ added.

it is not possible to unequivocally determine whether the resonances are due to two separate polymers or to i-PP/a-PP sequences in the same polymer chain. We have shown that the a-PP is a separate polymer by extraction of the total polymer sample (Entry 7, Table 4) into hot xylene, separation of the xylene solubles, and remeasuring the ¹³C NMR spectrum of the xylene insolubles. This showed appreciably less a-PP present (2% instead of 9%).

The activity of **6**/MAO increases from 200 to 576 kg/g Zr · h on increasing the polymerization temperature from 50 to 67°C. Comparison of entries 1 and 6, using 37 000 and 8000 equiv. of MAO respectively, indicates that in both cases, similar activities are obtained, suggesting that 8000 equiv. is sufficient for optimization of the activity of **6**. An increase in MAO:Zr ratio has been previously shown using Me₂Si(2-Me,4-Ph-indenyl)₂ZrCl₂/MAO to result in an increase of activity [17,18,47,48]. In comparing entries 1 and 6, the molecular weight (M_v) is lowered in the polymerizations with 37 000 equiv. MAO ¹⁶. We believe this is due to increased chain transfer to Al.

Performing the polymerization in the pres-

ence of 2 vol/vol% H₂ in the gascap ¹⁷ (50°C, 8000 equiv. MAO) gives an increase of activity from 184 to 321 kg/g Zr · h (compare entries 6 and 7). This degree of hydrogen activation ¹⁸ is less than that previously observed with Me₂Si(2-Me,4-Ph-indenyl)₂ZrCl₂/MAO [47] and *rac*-CH₂CH₂(indenyl)₂ZrCl₂/MAO [50].

2.5. Effect of bridge substituent

To determine the influence of the alkyl group on the phosphorus bridge (RP) on the polymerization activity the ⁱPr analogue ⁱPrP(2-Me,4-Ph-indenyl)₂ZrCl₂ (**7**) was prepared ¹⁹. Although we anticipated that an alkyl substituent on the phosphorus bridge might afford proportionally more *rac*-isomer than the 1:2 *rac:meso* ratio observed in phenyl-substituted **6**, the *rac:meso* isomer ratio for **7** was the same as for **6**. Under identical conditions, **7**/MAO was ca. 3–5 times as active for the polymerization of propene as **6**/MAO.

Similar to that found for the polymerizations

¹⁶ The very large Al:Zr ratios of up to 1:37 000 are a consequence of the high catalyst activity. To avoid potential run-away polymerizations only 1.0 μmol of metallocene was used (= 37 mmol MAO). The small amount of metallocene added therefore necessarily implies a large Al:Zr ratio.

¹⁷ The volume% H₂ in the gas cap (i.e., space in autoclave above is the LIPP) was continuously monitored by GC.

¹⁸ The activation effect of H₂ has been ascribed to a dormant site model [49].

¹⁹ We also attempted to prepare the MeP and ^tBuP analogues of **6**. With MePCL₂, the dianion Li₂[MeP(2-Me,4-Ph-indenyl)₂] could be prepared, however, we were unable to synthesize the zirconocene. With ^tBuPCL₂, the ligand ^tBuP(2-Me,4-Ph-indenyl)₂ could not be prepared, possibly because of steric hindrance between the bulky *tert*-butyl group and the 2-Me substituent of the indenyl.

Table 5
Isospecific polymerization of propene using *rac*/*meso*-¹PrP(2-Me,4-Ph-indenyl)₂ZrCl₂ (**7**)/MAO

Entry	Amt Zr (μ mol)	Al/Zr (total)	T_{pol} ($^{\circ}$ C)	Activity (kg/g Zr·h)	LVN (dl/g)	a-PP (%)
1	4	8186	30	188	8.16	n.d.
2	1	8004	50	495	7.26	5.0
3	1	8016	50	966 ^a	3.40	7.8
4	1	37600	50	1265	6.60	2.0

All polymerizations in 5 litres LIPP; 1 min pre-polymerization at 30 $^{\circ}$ C then polymerization for 1 h at the stated temperature.

^a2 vol/vol% H₂ added.

using **6**/MAO, the isotactic-PP (98 mol % mmmm pentads) formed from **7**/MAO has, for all Entries in Table 5, 99.5–99.6% 1,2 insertions and 0.5–0.4% 2,1 (only *erythro*) regioerrors. The a-PP arises from the *meso* isomer of **7**. The melting points of the i-PP are 157–160 $^{\circ}$ C.

Although the polymerizations are performed with a ca. 1:2 *rac*:*meso* isomer ratio of **6** and **7**, the reported activities are calculated on the basis of the *total* zirconium present. The inherent activity of the *rac*-isomer is therefore ca. 3 times higher than that reported here. Other variations in either the indenyl group or the substituent on phosphorus are possible and could lead to increased activity. In comparison, under identical conditions Me₂Si(2-Me,4-Ph-indenyl)₂ZrCl₂/MAO [47], activated by 37 000 equiv. MAO, polymerizes propene (LIPP, 50 $^{\circ}$ C) to i-PP with an activity of 5800 kg/g Zr·h (C.J.S., unpublished results). Coordination of MAO to the lone pair on phosphorus could lead to the lower activities observed with **6** or **7**. In-situ ³¹P NMR experiments to determine if MAO does indeed coordinate to the phosphorus lone pair were inconclusive. We have not attempted oxidation or quaternization of the phosphorus.

3. Conclusions

A new class of catalysts for the polymerization of propene has been synthesized. These are the first examples of phosphorus-bridged metal-

locenes. Depending on the chosen ligand framework, these phosphorus-bridged metallocenes allow the syndiospecific (**2**/MAO), aspecific (**4**/MAO), or isospecific (**5**, **6** or **7**/MAO) polymerization of propene.

Metallocene **2**, activated by MAO, affords s-PP with a molecular weight and stereoregularity similar to that obtained with known carbon-bridged catalysts. In contrast, silicon-bridged **3** gives s-PP of low molecular weight and poor syndiotacticity. These differences have been rationalized with the assistance of ab initio calculations.

Metallocenes **6** and **7**, activated by MAO, afforded i-PP with ca. 98% mmmm pentads at polymerization temperatures of 50–67 $^{\circ}$ C. The melting points were 156–160 $^{\circ}$ C and molecular weights (M_v) were 250,000–1 100 000. Activities of up to 580 kg i-PP/g Zr·h for **6**/MAO (LIPP, 67 $^{\circ}$ C, 37000 equiv. MAO) and 1265 kg i-PP/g Zr·h for **7**/MAO (LIPP, 50 $^{\circ}$ C, 37 000 equiv. MAO) were obtained. Performing the polymerizations under 2 vol/vol% H₂ led to a ca. 3-fold increase in activity and affords i-PP with molecular weight ($M_v = 200\ 000$ –300 000). Increasing the MAO:Zr ratio also gave increased activity and lower polymer molecular weight due to increased chain transfer to Al.

4. Experimental

4.1. Small scale propene polymerization in LIPP

Polymerizations were carried out in 1 litre LIPP, using compounds **1**–**5**/MAO. In the premix (in toluene) 500 molar equiv. of MAO was used and the premix kept at 20 $^{\circ}$ C in the drybox for a known time. The autoclave was then charged with 170–180 g of LIPP at 25 $^{\circ}$ C. Whilst stirring, the scavenger MAO, and then the premix, were injected into the autoclave. Pre-polymerization was performed for 5 min at 25 $^{\circ}$ C. Subsequently, the temperature was increased to (typically) 50 $^{\circ}$ C or 67 $^{\circ}$ C in ca. 10 min and the

polymerization was continued for 1 h at this temperature. Metallocenes **6** and **7** were tested in a 5 L autoclave in 1.6 kg LIPP at the stated temperature.

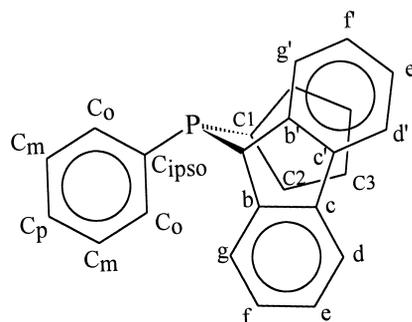
4.2. Preparation of PhP(Flu–Cp)ZrCl₂ (**2**)

(i) 3.03 g, 15.3 mmol PhP(OEt)₂ (³¹P NMR: δ 154 ppm) was added at 0°C to 2.79 g, 15.7 mmol PhPCl₂ (³¹P NMR: δ 160.5 ppm) in 35 mL diethylether. After stirring for 16 h at 25°C, 95% conversion to PhP(OEt)Cl (δ 174 ppm) was reached according to ³¹P NMR [36].

(ii) PhP(Flu–Cp): To the reaction mixture of PhP(OEt)Cl prepared above and cooled to –80°C was added an in-situ prepared solution of fluorenyllithium (from 4.87 g fluorene and 20 mL 1.6 M MeLi in hexane) in 50 ml ether. After 1.5 h at 0°C, conversion to PhPFlu(OEt) was complete (by ³¹P NMR). The mixture was cooled to –80°C and a solution of CpLi (2.09 g, 29 mmol) in 55 ml THF was added. The resulting solution was stirred overnight at 20°C, and then for 3 h at 40°C. After evaporation of the solvent, the solid was washed with a mixture of 40 ml hexane and 30 mL ether. Extraction with 100 ml ether afforded 3.72 g, 11 mmol PhP(Flu–Cp). ³¹P NMR: δ –14.4 ppm. It was contaminated with ca. 15% PhPFlu₂.

(iii) PhP(Flu–Cp)ZrCl₂ (**2**)

The PhP(Flu–Cp) from above was dissolved in 150 ml ether and excess *n*-BuLi (26 ml of a 1.6 M hexane solution) was added at 0°C. After stirring overnight at 20°C, a yellow precipitate of Li₂[PhPFluCp] formed. This was isolated by filtration, washed with hexane and dried to give 1.4 g of Li₂[PhPFluCp] (³¹P NMR: δ –52.3 ppm). 100 ml CH₂Cl₂, pre-cooled to –80°C, was added to Li₂[PhPFluCp], also cooled to –80°C. 0.94 g, 4 mmol ZrCl₄ was then added at –80°C and the reaction mixture gradually warmed to 25°C and stirred overnight. The solvent was removed in vacuum, and the solid extracted with 15 ml CH₂Cl₂. Careful addition of 20 ml hexane gave 0.64 g of PhP(Flu–Cp)ZrCl₂ as an orange powder. Cooling the



Scheme 1.

supernatant to –25°C yielded another 0.15 g product. Total yield of **2**, 0.79 g.

Analysis: Required for C₂₄H₁₇PZrCl₂. C 57.83; H, 3.44; P, 6.21; Zr, 18.30; Cl, 14.21. Found: C, 57.61; H, 3.56; P, 6.06; Zr, 18.05; Cl, 14.46. ³¹P NMR: δ –36.1 ppm.

A numbering scheme for ¹H and ¹³C NMR spectra of **2** is given in Scheme 1.

¹H NMR (CD₂Cl₂, 25°C): δ 8.09 (m, 1H, H_d), 8.05 (m, 1H, H_{d'}), 7.87 (m, 1H, H_{g'}), 7.76 (m, 2H, C_o), 7.59 (m, 1H, H_{e'}), 7.56 (m, 1H, H_e), 7.40 (m, 2H, C_m), 7.40 (m, 1H, C_p), 7.36 (m, 1H, H_{f'}), 6.94 (m, 1H, H_f), 6.51 (m, 1H, H_g), 6.48 (m, 1H, Cp), 6.44 (m, 1H, Cp), 5.98 (m, 1H, Cp), 5.91 (m, 1H, Cp).

¹³C NMR (CD₂Cl₂, 25°C): δ 133.8 (d, J_{CP} = 7, C_{b'}), 130.8 (d, J_{CP} = 15, C_o), 130.4 (d, J_{CP} = 31, C_{ipso}), 130.1 (d, J_{CP} = 1, C_{f'}), 129.6 (d, J_{CP} = 5, C_m), 129.5 (d, J_{CP} < 1, C_b), 129.0 (d, J_{CP} = 1, C_{para}), 128.4 (s, C_f), 127.2 (d, J_{CP} = 1, C_{e'}), 127.1 (s, C_e), 126.9 (s, Cp2), 125.9 (s, C_d), 125.8 (d, J_{CP} = 6, C_c), 125.1 (d, J_{CP} = 1, C_{d'}), 124.4 (d, J_{CP} = 1, C_g), 124.1 (d, J_{CP} = 9, C_{e'}), 123.9 (d, J_{CP} = 14, C_{g'}), 120.4 (d, J_{CP} = 11, Cp2'), 114.5 (d, J_{CP} = 40, Cp3'), 109.4 (d, J_{CP} = 8, Cp3), 95.1 (d, J_{CP} = 23, C_a), 60.5 (d, J_{CP} = 26, Cp1).

In contrast to the asymmetry seen in the NMR spectra of **2** caused by the PhP bridge, reference NMR spectra (¹H, ¹³C in CD₂Cl₂) of Me₂C(Flu–Cp)ZrCl₂ (**1**) show, as expected, a symmetrical ligand environment. ¹H NMR: δ 8.14 (d, 2H), 7.87 (d, 2H), 7.6 (t, 2H), 7.3 (t, 2H), 6.3 (m, 2H), 5.78 (m, 2H), 2.39 (s, 6H, Me). ¹³C NMR: δ 129.4 (2 × CH_{flu}), 125.4

($2 \times \text{CH}_{\text{flu}}$), 125.1 ($2 \times \text{CH}_{\text{flu}}$), 123.9 ($2 \times \text{CH}_{\text{flu}}$), 123.8 ($2 \times \text{C}_{\text{flu}}$), 123.2 ($2 \times 2\text{C}_{\text{flu}}$), 119.6 ($2 \times \text{C}_{\text{cp}}$), 115.6 ($\text{C}_{\text{ipso-flu}}$), 102.8 ($2 \times \text{C}_{\text{cp}}$), 80.5 ($\text{C}_{\text{ipso Cp}}$), 41.1 (CMe_2), 28.9 (CMe_2).

4.3. Preparation of $\text{Me}_2\text{Si}(\text{Flu}-\text{Cp})\text{ZrCl}_2$ (3) [38]

Fluorenyllithium was added to a 6 fold excess of Me_2SiCl_2 in ether cooled to -80°C , and the reaction mixture was slowly allowed to warm to 20°C . Ether was removed under vacuum, and replaced with THF. To this THF solution of $\text{FluSiMe}_2\text{Cl}$ (contaminated with ca. 10% $\text{Flu}_2\text{SiMe}_2$) was added 1 equiv. of CpLi at -80°C . After allowing to warm to 20°C , it was stirred for 16 h. The dianion $\text{Li}_2[\text{Me}_2\text{Si}(\text{Flu}-\text{Cp})]$ was prepared and isolated as a yellow powder. Reaction with ZrCl_4 in CH_2Cl_2 at -80°C gave $\text{Me}_2\text{Si}(\text{Flu}-\text{Cp})\text{ZrCl}_2$ (600 mg) as a pure orange crystalline product. ^1H NMR (C_6D_6): δ 8.1 (d, 2H), 7.6 (m, 4H), 7.3 (m, 2H), 6.54 (t, 2H, Cp), 5.79 (t, 2H, Cp), 1.11 (s, 6H, Me_2Si).

4.4. Preparation of $\text{PhP}(\text{Flu})_2\text{ZrCl}_2$ (4)

65 mL of a 1.6 M (104 mmol) solution of MeLi in ether was added dropwise at 20°C to 16.6 g, 100 mmol fluorene dissolved in 200 ml THF. The mixture turned rapidly yellow/orange and was stirred at 20°C for 2 h. This fluorenyllithium solution was cooled to -78°C and 8.75 g, 49 mmol PhPCl_2 was slowly (1 h) added. The solution was warmed slowly to 20°C and stirred for 60 h resulting in a yellow precipitate and a dark red-brown solution. The THF was removed in vacuum to give a sticky yellow-brown solid. This was washed with toluene (60 ml) and hexane (2×30 ml) to remove organic impurities. After drying in vacuum this gave 17.3 g of $\text{PhP}(\text{Flu})_2 \cdot \text{LiCl}$ as a bright yellow powder. ^{31}P NMR: δ 7.1 ppm. ^1H NMR: δ 5.14 (d, 2H, $J_{\text{PH}} = 4.3$ Hz, CH).

6.93 g $\text{PhP}(\text{Flu})_2 \cdot \text{LiCl}$ from above was dissolved in 100 ml THF at 0°C , and excess *n*-BuLi

(53 ml of a 1.6 M solution) was added. The yellow solution immediately turned dark red-brown. It was allowed to slowly warm to 20°C and stirred for 16 h. The solvent was removed under vacuum to give a yellow-brown solid which was washed with 3×20 ml hexane. After drying under vacuum 10.3 g of $\text{Li}_2[\text{PhP}(\text{Flu})_2] \cdot \text{LiCl}(\text{THF})_x$ as a yellow-brown powder was obtained. ^{31}P NMR: δ -72.5 ppm.

To 5.0 g of $\text{Li}_2[\text{PhP}(\text{Flu})_2] \cdot \text{LiCl} \cdot (\text{THF})_x$ was added 150 ml CH_2Cl_2 precooled to -80°C . 2.63 g, 11.3 mmol ZrCl_4 (unintentional excess) was added as a solid and the reaction mixture allowed to slowly warm to 20°C and stirred for 65 h at 20°C . This gave a dark red-brown mixture with a fine precipitate. The suspension was filtered and the CH_2Cl_2 removed in vacuum to give a sticky solid. This was washed with 20 ml toluene and 2×20 ml hexane to give **4** as a red powder. ^{31}P NMR: δ -44.7 ppm.

4.5. Preparation of $\text{PhP}(\text{indenyl})_2\text{ZrCl}_2$ (5)

4.5.1. $\text{PhP}(\text{indenyl})_2$

To a solution of 1.4 g, 12 mmol indene in 20 ml THF and cooled to -80°C was added 7.5 ml of a 1.6 M *n*-BuLi solution during 15 min. The mixture was allowed to warm to 20°C and stirred for 30 min. It was then added to 1.07 g, 6.0 mmol PhPCl_2 in 10 ml THF cooled to 0°C . The solution was allowed to warm in ca. 30 min to 25°C ; conversion was then complete, and solvents were removed in vacuo. The solid was extracted with toluene (20 ml), the toluene removed under vacuum, and the solid washed with hexane (10 ml) to yield a white/yellow solid which was characterized by ^1H , ^{31}P and ^{13}C NMR spectroscopy.

4.5.2. $\text{Li}_2[\text{PhP}(\text{indenyl})_2]$

$\text{PhP}(\text{indenyl})_2$ from above was dissolved in 10 ml THF, cooled to -5°C and 2 equiv. (15 ml of a 1.6 M solution) *n*-BuLi added during 20 min. The solution turned immediately dark red-brown. After allowing to warm to 20°C , it was stirred for another 2 h. The solvent was

removed and the resulting brown–red oil washed with 2×8 ml hexane. This afforded $\text{Li}_2[\text{PhP}(\text{indenyl})_2](\text{THF})_2$ as a yellow powder. ^1H NMR (d^8 -THF): δ 7.8 (d, 2H), 7.5 (m, 4H), 7.0–6.7 (m, 5H), 6.4 (m, 4H), 6.05 (br s, 2H). ^{31}P NMR (THF, 25°C): δ -54.5 ppm. ^{13}C NMR: δ 159.2 (s, 1C), 152.7 (d, $J_{\text{CP}} = 9.5$, 1C), 135.6 (d, $J_{\text{CP}} = 23$, 2C), 133.8 (d, $J_{\text{CP}} = 6.8$, 2C), 131.9 (d, $J_{\text{CP}} = 16$, $2 \times \text{CH}$), 126.5 (d, $J_{\text{CP}} = 4$, $2 \times \text{CH}$), 124.5 (d, $J_{\text{CP}} = 13$, $2 \times \text{CH}$), 123.6 (s, $1 \times \text{CH}$), 119.8 (d, $J_{\text{CP}} = 9$, $2 \times \text{CH}$), 119.0 (s, $2 \times \text{CH}$), 113.6 (d, $J_{\text{CP}} = 6$, $4 \times \text{CH}$), 97.8 (d, $J_{\text{CP}} = 7$, $2 \times \text{CH}$), 97.5 ppm (d, $J_{\text{CP}} = 6$, $2 \times \text{C}$).

4.5.3. *rac*-PhP(indenyl) $_2$ ZrCl $_2$ (5)

$\text{Li}_2[\text{PhP}(\text{indenyl})_2](\text{THF})_2$ from above was dissolved in 20 ml toluene, cooled to -30°C and 1.4 g, 6 mmol ZrCl_4 added, causing an immediate color change to dark red–brown. The reaction mixture was stirred at 20°C for 18 h. The LiCl precipitate was removed by centrifugation of the dark red–brown toluene solution. Evaporation of the solvent yields a 1:1 mixture of *rac*/*meso* isomers (^{31}P NMR: δ -35.2 and -45.3 ppm). Separation of *rac* and *meso* isomers was achieved by toluene/ether layer diffusion at -25°C . The resulting yellow–orange solid was washed with ether (5 ml). According to ^{31}P NMR this was ca. 95% of one of the isomers (^{31}P NMR δ -45.3 ppm). We assume this to be the *rac*-isomer from the stereoregularity of the polypropylene obtained in polymerizations.

4.6. Preparation of PhP(2-Me-4-Phindenyl) $_2$ ZrCl $_2$ (6)

To a solution of 0.22 g, 1.14 mmol 2-methyl-4-phenylindene in 6 ml toluene/THF (1:13) was added 0.7 ml *n*-BuLi (1.6 M in hexane, 1.12 mmol) at 20°C . This mixture was heated for 100 min at 80°C . The solvents of the dark red/brown mixture were removed and the beige/brown solid dissolved in 5 ml THF. This solution was added to 0.10 g PhPCl_2 (0.57

mmol) in 1.5 ml THF at 0°C . The color changed from dark red to light yellow. The reaction was complete after 5 min. The solvent was removed under vacuo and the resulting oil dissolved in 2 ml THF. To this solution of $\text{PhP}(2\text{-Me-4-Ph-indenyl})_2$ was added 0.7 ml *n*-BuLi (1.6 M in hexane, 1.12 mmol) was added in 5 min at -15°C . After stirring for 40 min at -15°C the solvent was removed under vacuo. The dark red di-anion $\text{Li}_2[\text{PhP}(2\text{-Me,4-Ph-indenyl})_2]$ was dissolved in 5 ml toluene and added to a slurry of 0.133 g, 0.57 mmol ZrCl_4 in 2 ml toluene at -70°C . The red solution was stirred for 75 min and the temperature raised to 0°C . The solvent was removed under vacuo and the resulting solid redissolved in 5 ml toluene. After removing LiCl by centrifugation the toluene was removed under vacuo. It was not possible to separate the *rac* and *meso* diastereoisomers and hence this mixture of $\text{PhP}(2\text{-Me,4-Ph-indenyl})_2\text{ZrCl}_2$ was used directly in the polymerizations.

$\text{Li}(2\text{-Me, 4-Ph-indenyl})$ (d^8 -THF): δ 2.36 (s, 3H), 5.81 (s, 1H), 6.01 (s, 1H), 6.51 (m, 2H), 7.25 (m, 4H), 7.84 (d, 2H).

$\text{PhP}(2\text{-Me, 4-Ph-indenyl})_2$ (d^8 -THF): δ 1.43 (s), 2.13 (s), 2.42 (s), 4.54 (s), 4.68 (s), 4.84 (s), 6.40 (s), 6.58 (s), 6.78 (s), 6.9–8.0 (m).

$\text{Li}_2[\text{PhP}(2\text{-Me, 4-Ph-indenyl})_2]$ ^1H NMR (d^8 -THF): δ 2.60 (s, Me). ^{31}P NMR (C_6D_6): δ -60.1 ppm.

Diastereoisomers of **6**. ^1H NMR (C_6D_6): δ 1.91 (s, Me), 2.33 (s, Me), 2.48 (s, Me), 6.4–6.6 (m, 2H), 6.8–8.0 (aromatic H's). ^{31}P NMR: δ -37.7 , -38.2 , -38.6 ppm.

4.7. Preparation of *i*PrP(2-Me-4-Phindenyl) $_2$ ZrCl $_2$ (7)

This was prepared in a similar fashion as that described above for **6**.

^1H NMR (C_6D_6): δ 1.2–1.3 (m, CHMe_2) 2.11 (s, Me), 2.27 (s, Me), 2.41 (s, Me), 6.4–6.6 (m, 2H), 6.8–8.0 (aromatic H's). The ^{31}P NMR shows three signals at δ -26.7 , -27.0 , -27.5 ppm in a ca. 1:4:1 ratio, respectively.

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