

Phospholyl catalysts for olefin polymerization

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Abstract

Seventeen different phospholyl ligands were incorporated in a total of 22 zirconium complexes, $(\text{Phos})_2\text{ZrCl}_2$, $(\text{Phos})(\text{C}_5\text{H}_5)\text{ZrCl}_2$, investigated in propylene polymerization catalysis using methylaluminumoxane as cocatalyst. Atactic polypropylene with M_n varying from 450 to > 20 000 and vinylidene end groups ($\text{CH}_2=\text{C}(\text{Me})\text{R}$) was obtained with activities up to 170 kg/g Zr · h. For the 11 diphospholyls of structure $(2,5\text{-R}_2\text{C}_4\text{H}_2\text{P})_2\text{ZrCl}_2$, catalytic activity was highest with substituents of moderate bulk adjacent to phosphorus (e.g., *c*-Pr, Ph), whereas complexes with two small (H) or two large (CMe_3 , SiMe_3) ligand substituents were inactive. It is hypothesized that optimum activity with MAO requires selective blocking of phosphorus lone pair coordination to aluminum, whilst allowing free propylene approach to the active site. The degree of polymerization increased steadily in the series of 2,5-disubstituted phospholyl complexes, dialkyl < alkyl-phenyl < diphenyl, suggesting that electronic factors are more important than steric factors in determining M_n . © 1998 Elsevier Science B.V.

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1. Introduction

The high activity and tunable stereo- and regioselectivity of metallocene-based olefin polymerization catalysts [1,2] has spawned an intensive academic and industrial effort to develop related catalysts in which one or both of the cyclopentadienyl groups is replaced by another ligand. Alternative unsaturated carbon-based ligands, based on the butadiene [3], penta-dienyl [4], benzene [5] or cyclooctatetraene [6]

fragments, as well as hard heteroatom-based ligands, such as amides [7–9] and alkoxides [10], have recently received much attention. The interest in and potential of five or six-membered heteroatom-containing rings is illustrated by studies of systems containing (amino)borolyl (C_4B ring) [11], azaborolyl (C_3BN ring) [12] and boratabenzene ligands (C_5B ring) [13,14]. We anticipated that phospholyl ligands, for which a well-established synthetic methodology and organometallic chemistry exists [15], as well as their analogues containing heavier group 15 elements, would allow a facile entry to a broad new family of heteroring-based polymerization catalysts.

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Unlike pyrolyl ligands, which, unless containing bulky substituents adjacent to the heteroatom, tend to distort towards η^1 -coordination of nitrogen to electrophilic metals [16,17], phospholyl ligands generally adopt a cyclopentadienyl-like η^5 -coordination [18,19]. Further, theoretical studies have indicated that phospholyl ligands exhibit similar electronic characteristics to cyclopentadienyl ligands [20,21]. A major difference between metallocene and phospholyl complexes is the presence of the phosphorus lone pair, which could play a non-innocent role in catalysis. For example, coordination to the Lewis acidic alkylaluminum cocatalyst might block the (cationic) active site and alter the ligand steric properties [20–22]. Alternatively, the formation of dimetallic complexes via well-precedented η^1, η^5 -bridging coordination of the phospholyl might result in catalyst deactivation [23]. Variation of the ligand steric bulk in the vicinity of phosphorus might, therefore, be expected to effect catalytic behaviour significantly. For this reason, and in order to allow a systematic study of ligand effects in phospholyl catalysis, a project was initiated to utilize existing methodology to synthesize a wide range of different phospholyl ligands and corresponding zirconium complexes.

Despite the fact that a range of phospholyl ligands is known, the number of different phospholyl ligands applied in Early Transition Metal chemistry is limited to three, C_4Me_4P , $3,4-Me_2C_4H_2P$ and C_4H_4P (the latter only in a mono-phospholyl Ti complex) [24–28], the major effort having been devoted to later transition metals [23,24]. Since the completion of this work [29], other, primarily Japanese, workers have reported studies and potential industrial application of group 4 phospholyl complexes in catalytic olefin polymerization [30–35]. However, this work of limited scope utilized only the narrow range of existing phospholyl complexes, with the greatest emphasis on ethylene (co)polymerization. Here we report the first systematic study of ligand effects in polymerization catalysis with phospholyl complexes [29].

One of the goals of this work was to study atactic oligo- and polypropylene formation. In contrast to the effort expended on isotactic and syndiotactic polypropylene, aspecific polymerization with metallocenes has received much less attention [1,2,36]. Metallocene-derived atactic polypropylene might replace the material previously formed as a by-product in Ziegler–Natta polymerization and incorporated in bitumen and hot melt adhesives, whereas low molecular weight atactic propylene oligomers (APO's) may afford interesting new materials via the functionalization of the unsaturated end group [36–44]. Regioselective propylene polymerization (1,2-insertion) most commonly affords vinylidene end groups, $CH_2=C(Me)R$, by β -hydrogen elimination/transfer; vinyl end groups, $CH_2=CHCH_2C(Me)R$, are obtained by β -methyl elimination with certain sterically crowded metallocenes [42–44]. Functionalization of vinylidene-capped APO's (with polar functionalities or aluminum) [37–41] has afforded oligomers, which may, for example, be used for block copolymer formation. Vinyl-capped APO's have found use as monomers in copolymerization [37–41]. We believed that by appropriate control of the steric and electronic environment in phospholyl complexes, we could tune the activity, product molecular weight and end groups in atactic propylene oligo/polymerization.

2. Preparation of phospholylzirconium complexes

Phospholyl complexes of zirconium were obtained in three steps from dienes or diynes following modified literature procedures [15]. The initially formed 1-phenylphosphole precursor is reduced to the phospholyl anion, followed by reaction with an appropriate zirconium dihalide to give diphospholyl or mono-phospholyl complexes. Although a full discussion of the syntheses is outside the scope of this article, an overview of the synthetic methods utilized is

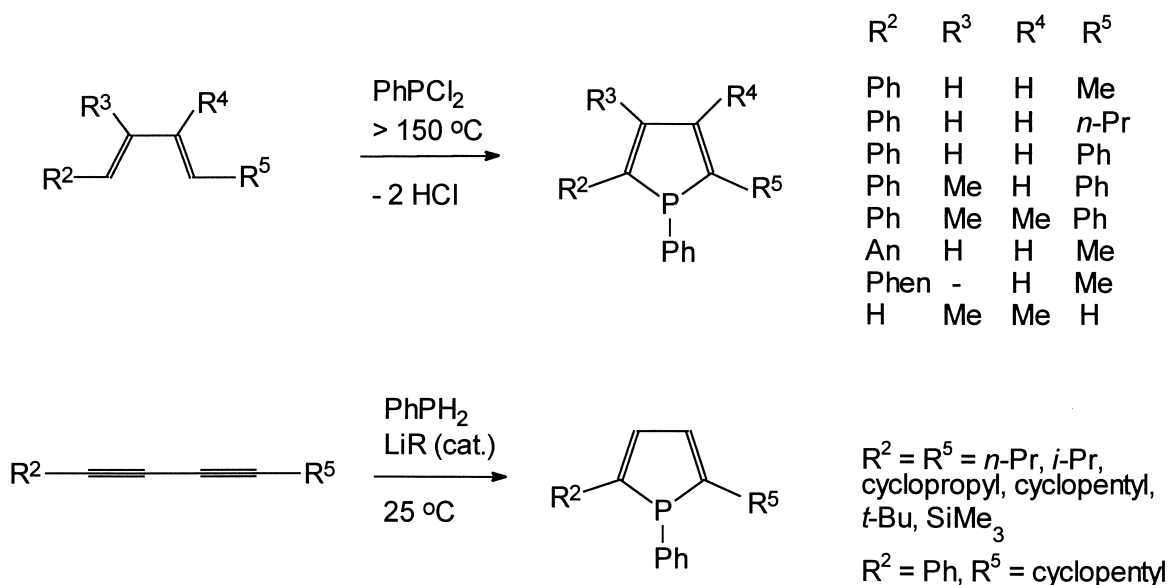


Fig. 1. Synthetic routes to 1-phenylphospholes.

given below. The preparation of four representative diphospholyl complexes is described in Section 2¹.

Anionic phospholyl ligands are most conveniently obtained from the corresponding 1-phenylphosphole by reductive cleavage of the P–Ph bond [15]. Two general routes to substituted 1-phenylphospholes, which allow facile substituent variation, have been utilized (Fig. 1):

(i) Reaction of 1,3-dienes with PhPCl₂ under forcing conditions with HCl elimination [15].

(ii) Direct addition of PhPH₂ to 1,3-diyne at ambient temperatures using a lithium hydrocarbyl catalyst [45–47].

Whereas the diene route permits the synthesis of phospholyl ligands with up to four substituents, the diyne route is restricted to 2,5-disubstituted derivatives. However, a significant

advantage of the latter method is the use of mild experimental conditions [45–47]. This obviates the phenyl/alkyl scrambling between phosphorus and carbon (via a concerted 1,5-hydrocarbyl shift) which can lead to mixtures of phospholes at the high temperatures (150–200°C) used in the diene route [48]. An additional disadvantage of the diene route is that the permitted substituents are limited to phenyl groups and small alkyl groups [15]. Prior to this work, the diyne route had been applied to the synthesis of only a limited range of phospholyl ligands [45–47]. The known 1-phenylphospholes, C₄Me₄PPh [24] and C₄Ph₄PPh [15], were obtained by alternative routine literature procedures, without general applicability.

Zirconium complexes with 17 different phospholyl ligands were obtained, as shown in Fig. 2, by reductive cleavage of the P–Ph bond of the 1-phenylphosphole, followed by reaction of the phospholyl anion with ZrCl₄ or, for mixed complexes, (C₅H₅)ZrCl₃. The phenylalkali byproduct of the reaction of the phenylphosphole with excess lithium or sodium was normally quenched by reaction with *t*-BuCl (1.0 equivalent) or AlCl₃ (1/3 equivalent). The crude

¹ Synthetic details are contained in Ref. [29]. Characterization of new phospholyl complexes has included X-ray structural studies, which will be published elsewhere. These studies show that complexes with two crowded 2,5-disubstituted phospholyl ligands exhibit bent metallocene structures with the phosphorus atoms at the open end of the wedge formed by the two rings. In contrast in (C₄Me₄P)₂ZrCl₂, the phosphorus atoms are located at the back end of the wedge [24].

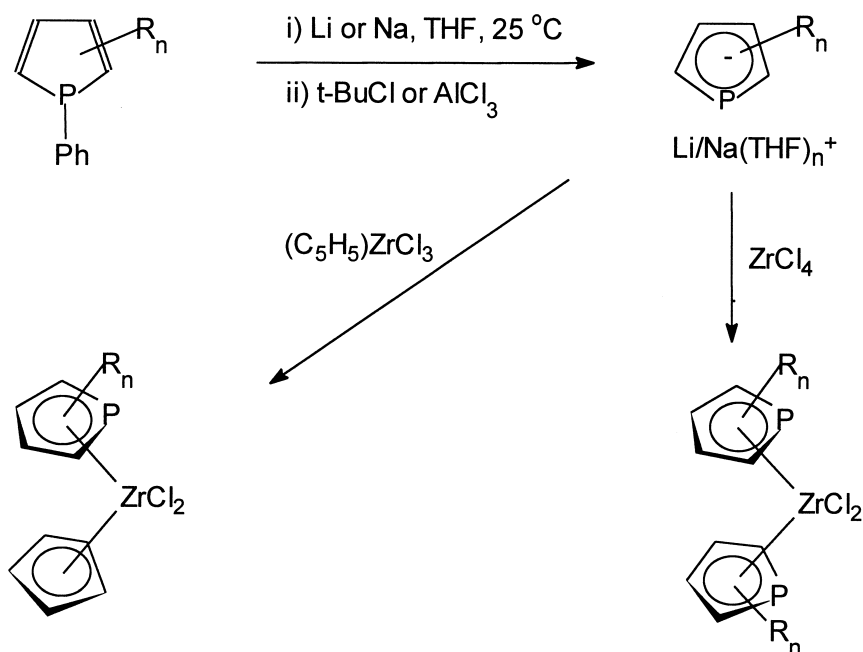


Fig. 2. Synthesis of zirconium phosphohyl complexes.

phosphohyl anion (contaminated with LiCl or NaCl), was generally obtained as a spectroscopically pure (^{31}P -NMR) solid after extraction and washing steps. Zirconium complex formation was carried out in toluene, diethyl ether or mixtures of these solvents. The generally spectroscopically pure (^{31}P -NMR) solid yellow or orange complexes, obtained by solvent extraction of the crude residue, reduction to dryness and washing with hexane, were used directly for polymerization testing, without further recrystallization. Yields of isolated diphosphohyl complexes in the range 10–50% (based on starting 1-phenylphosphole) were obtained.

3. Propylene polymerization

The major goal of this investigation was to study the effect of ligand variation on the polymerization activity and product structure in phosphohylzirconium catalysis. As already discussed, APO's containing a vinylidene end

group are of interest for a range of applications. The oligo/polymerization of propylene (600 kPa) was investigated under standard conditions in toluene solution (45°C, 10–60 min) using MAO as cocatalyst. The amounts of zirconium complex (10 μ mol) and MAO (5.0 mmol aluminum) used resulted in an Al/Zr ratio of 500 and an aluminum concentration of 22.4 mM. Under the polymerization conditions, the generally atactic product is soluble in toluene. The advantage of studying a truly homogeneous polymerization is that complications caused by polymer precipitation (e.g., catalyst deactivation on heterogenization), can be avoided and activity comparisons of different catalysts are expected to be more meaningful.

3.1. Catalytic activity

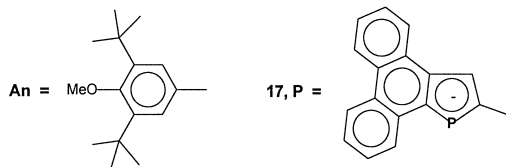
Of the seventeen diphosphohyl complexes examined, twelve afforded atactic (or near-atactic, see below) polypropylene or propylene oligomers and five were catalytically inactive.

Table 1
Propylene polymerization activity of phospholylzirconium complexes

Complex	Type	Substituents				Activity (kg/gZr · h)	M_n
		R ²	R ³	R ⁴	R ⁵		
1	P ₂ Zr	H	Me	Me	H	—	—
2	P ₂ Zr	Me	Me	Me	Me	—	—
3	P ₂ Zr	<i>n</i> -Pr	H	H	<i>n</i> -Pr	8.1	1 600
4 ^a	P ₂ Zr	<i>i</i> -Pr	H	H	<i>i</i> -Pr	36.4	1 400
5	P ₂ Zr	<i>c</i> -Pr	H	H	<i>c</i> -Pr	104.2	4 100
6	P ₂ Zr	<i>c</i> -Pe	H	H	<i>c</i> -Pe	115.3	1 500
7 ^a	P ₂ Zr	<i>t</i> -Bu	H	H	<i>t</i> -Bu	—	—
8	P ₂ Zr	Me ₃ Si	H	H	Me ₃ Si	—	—
9	P ₂ Zr	Ph	H	H	Me	92.2	6 700
10	P ₂ Zr	Ph	H	H	<i>n</i> -Pr	83.0	5 100
11	P ₂ Zr	Ph	H	H	<i>c</i> -Pe	108.8	4 600
12	P ₂ Zr	Ph	H	H	Ph	169.6	> 20 000
13	P ₂ Zr	Ph	Me	H	Ph	82.9	20 000
14	P ₂ Zr	Ph	Me	Me	Ph	15.2	450
15	P ₂ Zr	Ph	Ph	Ph	Ph	—	—
16	P ₂ Zr	An	H	H	Me	55.3	7 500
17	P ₂ Zr	Phen	—	H	Me	32.2	> 20 000
18	P(Cp)Zr	H	Me	Me	H	—	—
19	P(Cp)Zr	Me	Me	Me	Me	—	—
20	P(Cp)Zr	<i>t</i> -Bu	H	H	<i>t</i> -Bu	7.8	1 400
21	P(Cp)Zr	Ph	H	H	Ph	64.5	1 700
22	P ₂ Zr.W ₄ (CO)	Me	Me	Me	Me	4.6	3 000

Standard conditions: 10.0 μmol Zr, 5.0 mmol MAO (^acomplexes **4** and **7**: 20.0 μmol Zr, 10.0 mmol Al), total volume toluene 223.5 ml, pressure propylene 600 kPa, temp. 45°C, polymerization time 10–60 min. M_n and end group content determined by ¹H-NMR studies of isolated product.

P₂Zr = (Phos)₂ZrCl₂; P(Cp)Zr = (Phos)(C₅H₅)ZrCl₂; *c*-Pe = cyclopentyl



Examination of the data in Table 1 shows that the catalytic activity exhibits a remarkable dependence on the steric bulk of the substituents of the phospholyl rings. The presence of two hydrocarbyl substituents adjacent to phosphorus, the larger of which is of intermediate steric bulk (phenyl or CHR₂), appears to be necessary for optimum catalytic activity. For example, the increased activity in the series of complexes **3–6**, with 2,5-dialkyl-phospholyls, 2,5-R₂C₄H₂P, (R =) *n*-Pr < *i*-Pr < *c*-Pr = *c*-Pe, correlates with increased effective steric bulk.

Complexes **9–11**, with 2-alkyl,5-phenylphos-

pholyl ligands, exhibit high activities in a narrow range (in contrast to the greater variation found for **3–6**). These complexes, are, however, significantly less active than the 2,5-diphenylphospholyl complex, **12**, perhaps reflecting the effect of differences in electron-donating abilities of phenyl and alkyl substituents. Complex **12** exhibits the highest activity of all complexes tested. Phospholyls with two very bulky substituents adjacent to phosphorus (*t*-butyl [47], trimethylsilyl) are inactive. Similarly, a continuous decrease in activity as the degree and total bulk of substitution increases is observed in the

series of complexes **12–15** (activity: $\text{Ph}_2 > \text{Ph}_2\text{Me} > \text{Ph}_2\text{Me}_2 > \text{Ph}_4$). The result obtained with crowded complex **15** is consistent with the catalytic inactivity of the metallocene analogue, $(\text{C}_5\text{Ph}_4\text{H})_2\text{ZrCl}_2/\text{MAO}$ [49]. The inactivity of the 3,4-dimethylphospholyl complex, **1**, and the 2,3,4,5-tetramethylphospholyl complex, **2**, again underlies the apparent necessity for intermediate steric bulk in the phospholyl adjacent to phosphorus; this seems to be more important than ‘total’ ligand steric bulk for activity (the $\text{Me}_4\text{C}_4\text{P}$ ligand may, in cyclopentadienyl terms, be considered bulky).

Catalytic activity in the mixed phospholyl-cyclopentadienyl complexes **18–21** shows a similar sensitivity to the steric bulk adjacent to phosphorus. The 2,5-diphenylphospholyl complex is much more active than the *t*-butyl analogue, whilst the methyl-substituted phospholyl complexes are inert. Bridging coordination of $\text{W}(\text{CO})_4$ between the two tetramethylphospholyl ligands in complex **22** results in increased (albeit low) activity compared to complex **2**. This may reflect ‘protection’ of the phosphorus atom from interaction with aluminum, although the carbonyl tungsten fragment might be expected to react with MAO under the polymerization reaction conditions.

3.2. Degree of polymerization

In contrast to the strong dependence of activity on the steric properties of the phospholyl ligand, the degree of polymerization found for the diphospholyl complexes appears to be closely linked to the electronic properties of the phospholyl substituents. For the nine active 2,5-disubstituted complexes, the molecular weight increases in the series dialkyl < alkyl, phenyl < diphenyl. This trend, with M_n increasing from 1400–4100 (**3–6**), to 4600–7500 (**9–11**) to values greater than 20 000 (**12**, **17**), appears to reflect decreased electron-donation to the heteroatom ring.

The one complex which, although fitting the trend, does not do so elegantly, is 2,5-dicyclopropylphospholyl **5**. The higher M_n of

4100, compared to 1400–1600 for the other 2,5-dialkylphospholyl complexes, is consistent with conjugative interaction of the cyclopropyl ring with the heteropentadienyl ligand, which affords to the cyclopropyl group electronic properties intermediate between an alkyl and a phenyl group. The π -interaction of two cyclopropyl (ring-)C–C bonding orbitals with the aromatic ring is expected to be optimized by a perpendicular orientation of the two rings [50]. Stabilization of such a conformation may increase the effective steric bulk of the ligand compared to the di-isopropyl analogue, in which the methyl substituents likely point away from the zirconium atom. This in turn may partly explain the three-fold increase in activity from the isopropyl complex **4** to the cyclopropyl analogue **5**.

A decrease in M_n with increased methyl substitution is observed in the series of complexes **12–14** (substituents: Ph_2 , Ph_2Me , Ph_2Me_2 , respectively), but it is not clear whether this is a steric or electronic effect. Interestingly, dibenzophosphaindene complex **17** affords relatively higher molecular weight polypropylene than **9–11**, despite the fact that it contains an alkyl substituent adjacent to phosphorus.

Substituent effects on molecular weight in the mixed phospholyl-cyclopentadienyl complexes appear to be less pronounced, with complexes **20** and **21**, with *t*-butyl and phenyl substituents, respectively, at the 2,5-positions, affording APO's with similar M_n . The range of complexes studied is, however, too small, to allow firm conclusions to be drawn.

3.3. End groups and stereoregularity

The propylene oligomers ($M_n < 20\,000$) exhibit $^1\text{H-NMR}$ resonances (> 95%) for vinylidene end groups ($\text{CH}_2=\text{C}(\text{Me})\text{R}$), as expected for a process of chain termination involving β -hydrogen elimination or transfer to monomer. Resonances for vinyl end groups ($\text{CH}_2=\text{CHCH}_2\text{CH}(\text{Me})\text{R}$) or internal olefins are not observed. Certain sterically crowded metallocenes have been shown to undergo chain ter-

mination by β -methyl elimination, with the proportion of vinyl end groups increasing in the order $(C_5Me_4H)_2ZrCl_2 < (C_5Me_4H)(C_5Me_5)_2ZrCl_2 < (C_5Me_5)_2ZrCl_2$ [36,42–44]. The absence of vinyl end groups in the phospholyl catalysis reported here shows that, despite the high steric crowding of some of the active complexes (e.g., **14**, **22**), β -methyl elimination does not occur to a significant degree.

C_2 -symmetric diphospholyl complexes might be expected to exhibit some degree of isospecificity in propylene oligo/polymerization. Complexes **9–11**, **13** and **17** are present as mixtures of *rac* and *meso* isomers, as reflected in the observation of two distinct ^{31}P -NMR resonances. ^{13}C -NMR analysis of the methyl region showed that the propylene oligomers are, in general, atactic with *m:r* dyad ratios close to the ideal value of 50:50. In the case of complex **17**, slight isospecificity was found, with a *m:r* dyad ratio of 60:40. Given that **17** consists of an approximately equimolar mixture of *rac* and *meso* isomers, and (tentatively) assuming equal activities, it may be proposed that the *rac* isomer affords polymer with a *m:r* ratio of 70:30. The generally low or negligible stereospecificity of the *rac* isomers in propylene oligo/polymerization compares with previous studies of non-bridged metallocenes with 1-hydrocarbylindenyl ligands, in which (limited) stereospecificity was observed in certain cases in low temperature polymerizations [51]. It is possible that the unsymmetrically substituted phospholyl complexes may exhibit higher stereospecificity at polymerization temperatures far below that used in this study.

4. Discussion and conclusions

A certain degree of steric bulk adjacent to phosphorus in the phospholyl ring appears to be necessary for activity in phospholylzirconium catalysis. Of the 17 diphospholyl complexes tested to date, the highest activity is observed

when at least one, and preferably two of the substituents at the 2,5-positions of the phospholyl ring is a secondary hydrocarbyl group. Sufficient steric bulk adjacent to phosphorus may be required to suppress lone pair coordination to Lewis acidic aluminum centers in MAO [20–22]. Such coordination could block the approach of propylene monomer to the active site, or, alternatively, lead to phospholyl transfer to aluminum. Very large substituents (tertiary atoms on ring) shield not only the phosphorus, but also the active zirconium center and lead to inactive catalysts².

In contrast to the case for $(C_4Me_4P)_2ZrCl_2/MAO$, which is catalytically inactive for propylene (but active for ethylene), we have shown in other studies that the MAO-free cationic analogue, $[(C_4Me_4P)_2ZrMe]^+[A]^-$ ($[A]^-$ is a poorly coordinating anion), does polymerize propylene (albeit with only moderate activity) [29]³. This suggests that cationic diphospholyl complexes, similar to cationic metallocenes, should, intrinsically, exhibit activity for propylene polymerization, provided side reactions (such as aluminum coordination) can be blocked.

The clear effect of the electronic nature of the phospholyl substituents on the degree of polymerization of propylene, most clearly reflected in the series of 2,5-disubstituted-phospholyls (M_n increases: dialkyl < alkyl-phenyl < diphenyl), is remarkable. Some previous studies of electronic effects on metallocene polymerization indicated that the presence of

² It might be argued that the inactivity of complexes with bulky phospholyl ligands is due to a reduced rate of cationic alkylzirconium complex formation. However, we have found that cationic derivatives of complex **7** are instantaneously obtained on methyl-abstraction from the dimethyl precursor using normal borane/borate reagents: A.D. Horton and A.J. van der Linden, to be published.

³ The system, $(C_4Me_4P)_2ZrCl_2 / AlR_3 / [PhMe_2NH][B(C_6F_5)_4]$, in which a cationic alkyl species is presumably generated in situ, is reported to exhibit propylene polymerization activity [33]. In contrast to our findings, other workers have claimed (low) propene polymerization activity for the system, $(C_4Me_4P)_2ZrCl_2 / MAO$ [32,33].

electron-withdrawing substituents results in a lowering of polymer molecular weight (and activity), provided the ligand steric bulk in the immediate vicinity of the metal is relatively invariant [52–54]. There is no obvious explanation for the observation of a reverse trend in M_n in diphospholyl catalysis. It is especially surprising that steric bulk plays such a subsidiary role to the electronic nature of the substituents, as shown by the observation of similar M_n values for dialkyl complexes **3**, **4** and **6** (*n*-Pr, *i*-Pr and cyclopentyl substituents, respectively) and the significantly higher M_n for 2,5-dicyclopropylphospholyl complex **5** (proposed to be electronically intermediate between alkyl and phenyl).

This study has shown both the potential of phospholyl complexes as alternatives to metallocenes in polymerization catalysis and the importance of extensive ligand variation in tuning the catalytic properties. In this context, the inactivity of pre-existing diphospholylzirconium complexes for propylene polymerization (with MAO) should be noted³. Variation of the phospholyl substitution pattern has allowed polypropylene products to be obtained with molecular weights varying over a wide range and, in some cases, with high metallocene-like activities. Comparison of this programme of ligand variation to the much more extensive investigations of cyclopentadienyl ligand modification suggests that further studies may lead, for example, to stereospecific phospholyl catalysts. Extension of this concept of ligand substituent variation to pyrolyl, arsoly and other hetero-ring ligands is also likely to lead to new catalyst families⁴.

⁴ We have found that tetrahydrocarbazole ($C_{20}H_{16}N$) complexes, L_2ZrCl_2 and $L(C_5H_5)ZrCl_2$, and the arsoly complex, $(C_4Me_4As)(C_5H_5)ZrCl_2$, exhibit propylene polymerization activity with MAO [29].

5. Experimental details

5.1. General procedures

Preparative experiments were performed under nitrogen in a Braun MB 200-G dry box or under argon using standard Schlenk techniques. Solvents were dried by refluxing over and distilling from standard reagents. NMR solvents were dried over 4 Å molecular sieves. Propylene was purified over $AlEt_3$. Dienes were obtained from commercial suppliers (1,4-diphenyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene) or following literature procedures: in general, reaction of *trans*-cinnamaldehyde (or appropriate substituted derivatives) with a Grignard reagent afforded an unsaturated alcohol, which was then dehydrated using *para*-toluenesulphonic acid [55,56]. 1,4-diphenyl-2,3-dimethyl-1,3-butadiene was obtained from the reaction of 2,3-butadiene with benzylmagnesium chloride, followed by dehydration of the resulting diol [57]. 1,3-diynes, as well as other reagents, were either obtained from commercial suppliers and used without further purification or prepared by straightforward literature routes. ³¹P-NMR spectra were recorded on Varian XL-200 or VXR-300 (80.96 or 121.14 MHz, respectively). NMR data were recorded at 25°C and are listed in parts per million, referenced relative to $P(C_6H_5)_3$ in $CDCl_3$ (δ –6.0 ppm).

5.2. Typical preparations of diphospholyl complexes

Four representative syntheses of diphospholylzirconium complexes are presented below. Full details of the preparation and characterization of the new complexes (¹H, ¹³C, ³¹P-NMR, elemental analysis, X-ray structural studies) are discussed elsewhere [29] (see ¹). The syntheses are non-optimized and the isolated yields vary in the range 10–50%. Emphasis was placed on

obtaining pure complexes for catalytic testing, rather than on optimum yields. As the isolation of the complexes in pure form often relies on crystallization, the yields depend crucially on the complex solubility.

5.3. Preparation of $(2,5\text{-Ph}_2\text{-3-MeC}_4\text{HP})_2\text{ZrCl}_2$ (**13**)

1,4-Diphenyl-3-methyl-1,3-butadiene (9.1 g, 41.4 mmol), was allowed to react with PhPCl_2 (11.2 g, 62.6 mmol) for 17 h at 170°C under a slow argon flow. Subsequently, the reaction mixture was cooled to 25°C and 50 ml of dichloromethane was added. After further cooling of the obtained reaction mixture to 0°C , water was added slowly and the organic layer was separated and dried. The obtained residue was dissolved in a small amount of toluene and chromatographed over silica. Initially petroleum ether 80/110 was used as eluent and during elution progressively more toluene was introduced. The first fractions were mainly organic by-products, followed by a fraction containing 1.3 g of spectroscopically pure 1,2,5- $\text{Ph}_3\text{-3-MeC}_4\text{HP}$ ($^{31}\text{P-NMR}$, CDCl_3 , δ 11.9 ppm).

1,2,5- $\text{Ph}_3\text{-3-MeC}_4\text{HP}$ (0.64 g, 2.0 mmol) was dissolved in THF (40 ml) and reacted with excess lithium. The reaction mixture was stirred for 45 min, excess lithium was removed by filtration, and *t*-BuCl (0.5 ml) then added, followed by warming to 55°C and stirring for 30 min. Subsequently the volatiles were removed in vacuo and the residue dissolved in diethyl ether (30 ml). This solution was cooled to -78°C and then a suspension of ZrCl_4 (0.22 g, 0.94 mmol) in toluene (10 ml) was added. The stirred reaction mixture was allowed to warm to room temperature, the solvent removed in vacuo and the solids taken up in diethyl ether and passed through a short silica column. The solvent was removed and the residue washed with hexane and dried under vacuum to yield a mixture of *rac* and *meso* isomers of $(2,5\text{-Ph}_2\text{-3-MeC}_4\text{HP})_2\text{ZrCl}_2$ ($^{31}\text{P-NMR}$, CD_2Cl_2 , δ 87.2 and 83.2 ppm).

5.4. Preparation of $(2\text{-}(4\text{-MeO-3,5-}t\text{-Bu}_2\text{C}_6\text{H}_2)\text{-5-MeC}_4\text{H}_2\text{P})_2\text{ZrCl}_2$ (**16**)

1-(4-MeO-3,5-*t*-Bu₂C₆H₂)-1,3-pentadiene (5.3 g, 18.5 mmol), was allowed to react with PhPCl_2 (5.0 g, 27.8 mmol) for 16 h at 140°C , followed by 5 h at 150°C , under a slow argon flow. Subsequently, the reaction mixture was cooled to 25°C , dissolved in hexane and eluted over a silica column with hexane. The solvent was removed in vacuo and the volatile organic impurities removed by distillation at 200°C , leaving 2.4 g of non-volatile product, 1-Ph-2-(4-MeO-3,5-*t*-Bu₂C₆H₂)-5-MeC₄H₂P.

The above phenylphosphole was converted to 2-(4-MeO-3,5-*t*-Bu₂C₆H₂)-5-MeC₄H₂PNa(THF)_{*n*} by reaction with excess sodium, followed by quenching with *t*-BuCl. To a suspension of the anion (1.47 mmol) in toluene at 25°C was added a suspension of ZrCl_4 (0.17 g, 0.73 mmol) in toluene (10 ml) at 25°C . Subsequently the mixture was centrifuged and the clear orange solution decanted. The solution was reduced to dryness in vacuo and the solid extracted with hexane. On cooling the hexane solution to -20°C , orange crystals of spectroscopically pure product were obtained ($^{31}\text{P-NMR}$, CD_2Cl_2 , δ 83.0 ppm). It is not clear whether the product is the *rac* or the *meso* isomer.

5.5. Preparation of $(2,5\text{-Ph}_2\text{C}_4\text{H}_2\text{P})_2\text{ZrCl}_2$ (**12**)

1,2,5- $\text{Ph}_3\text{C}_4\text{H}_2\text{P}$ was prepared by a literature route [15] and converted to 2,5- $\text{Ph}_2\text{C}_4\text{H}_2\text{PNa(THF)}_n$ by reaction with excess sodium, followed by quenching with *t*-BuCl. To a suspension of the anion (2.3 mmol) in toluene (40 ml) at 25°C was added a suspension of ZrCl_4 (0.26 g, 1.14 mmol) in toluene (10 ml) at 25°C . After stirring for 2 h the mixture was warmed to 50°C and stirring was continued for another 0.5 h. Subsequently the mixture was centrifuged and the clear orange solution decanted and cooled to -20°C , yielding orange crystals (0.33 g) of product ($^{31}\text{P-NMR}$, CD_2Cl_2 , δ 83.1 ppm).

5.6. Preparation of $(2,5-t\text{-Bu}_2\text{-C}_4\text{H}_2\text{P})_2\text{ZrCl}_2$ (7)

PhPH₂ (5.0 g, 45.5 mmol) was added to a solution consisting of benzene (25 ml), THF (4 ml) and 4 ml of a 1.6 M solution of *n*-BuLi in hexane (6.4 mmol). 2,2,7,7-Tetramethyl-3,5-octadiyne (7.4 g, 45.5 mmol) was slowly added to the reaction mixture at 0°C. The resulting red suspension was stirred at 25°C for 24 h. Water was added after which the organic layer was separated and the volatiles removed in vacuo. The resulting slightly impure oil was used for further experiments (³¹P-NMR, C₆D₆, δ -1.1 ppm).

To a solution of the 2,5-di-*t*-butyl-1-phenylphosphole (4.5 ml) in THF (50 ml) was added excess Li. After 2 h, ³¹P-NMR spectroscopy showed the reaction to be complete and the excess lithium was filtered off. *t*-BuCl (2.5 ml) was added and the solution was heated for 1 h at 60°C. A yellow solid (2.6 g) was obtained after removal of the solvent *in vacuo* and washing the resultant residue with hexane (twice), shown by NMR spectroscopy to be $(2,5-t\text{-Bu}_2\text{-C}_4\text{H}_2\text{P})\text{Li}(\text{THF})_2$ contaminated with one equivalent of LiCl (³¹P-NMR, THF-d₈, δ 62.5 ppm).

To a suspension of $(2,5-t\text{-Bu}_2\text{-C}_4\text{H}_2\text{P})\text{Li}(\text{THF})_2$ (4.4 mmol) in diethylether (20 ml) at -40°C, was added ZrCl₄ (0.46 g, 2.0 mmol) and the suspension warmed to 25°C and stirred for 1 h. The yellow precipitate was separated by filtration and then extracted with CH₂Cl₂. After evaporation of the CH₂Cl₂, $(2,5-t\text{-Bu}_2\text{-C}_4\text{H}_2\text{P})_2\text{ZrCl}_2$ (0.12 g, 15%) was obtained as yellow microcrystals (³¹P-NMR, CD₂Cl₂, δ 100.7 ppm).

5.7. Polymerization reactions

A 1 l steel jacket-cooled autoclave, equipped with magnetic stirring and a catalyst injection device, was heated to 90°C, evacuated for 2 h, and subsequently pressurized and flushed three times with dry nitrogen. The reactor was cooled to 45°C and charged with 200 ml of toluene, 3.5

ml of a toluene solution containing 10% MAO (5.0 mmol), and then pressurized with 600 kPa of propylene. The system was allowed to reach equilibrium while the pressure was maintained at 600 kPa. Subsequently, $(2,5\text{-Ph}_2\text{C}_4\text{H}_2\text{P})_2\text{ZrCl}_2$ (10.0 μmol), dissolved in toluene (10 ml), was added to the autoclave by means of the catalyst injection system. The injection system and catalyst supply vessel were washed with toluene (10 ml), which was also added to the autoclave. After 14 min the reaction was stopped by rapid release of excess of propylene, and opening of the autoclave. After work-up, 38 g of product was obtained, shown by ¹H and ¹³C-NMR analysis to be atactic polypropylene with $M_n > 20\,000$.

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