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P–H functionalised phosphinoalkoxides as ligands: synthesis and catalytic properties of [$Cp_2Zr(Me)$(*cyclo*-1-O-2-PH(Tipp)-C_6H_{10})] (Tipp = 2,4,6-$Pr^i_3C_6H_2$), [$Cp_2Zr(Me)$(*cyclo*-1-O-2-PH(Tipp){$Mo(CO)_5$}–C_6H_{10})] and [$Cp_2Zr(BH_4)$(*cyclo*-1-O-2-PH(Mes)(BH_3)–C_6H_{10})] (Mes = 2,4,6-$Me_3C_6H_2$), and molecular structure of (R_C,R_C,R_P/S_C,S_C,S_P)-[$Cp_2Zr(Me)$(*cyclo*-1-O-2-PH(Tipp)–C_6H_{10})]☆

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Abstract

The P–H functionalised phosphinoalcohol 1-PH(Tipp)-2-OH-*cyclo*-C_6H_{10} (Tipp = 2,4,6-$Pr^i_3C_6H_2$) reacts with [Cp_2ZrMe_2] with elimination of methane to give exclusively the mono-substituted product [$Cp_2Zr(Me)$(*cyclo*-1-O-2-PH(Tipp)–C_6H_{10})] (**1**), even at elevated temperature. **1** reacts with [$Mo(CO)_5(NMe_3)$] to give the heterodinuclear complex [$Cp_2Zr(Me)$(*cyclo*-1-O-2-PH-(Tipp){$Mo(CO)_5$}–C_6H_{10})] (**2**). The borane adduct [$Cp_2Zr(BH_4)$(*cyclo*-1-O-2-PH(Mes)(BH_3)–C_6H_{10})] (**3**, Mes = 2,4,6-$Me_3C_6H_2$) was obtained from [$Cp_2Zr(BH_4)_2$] and 1-PH(Mes)-2-OH-*cyclo*-C_6H_{10} in boiling hexane. **1**–**3** were characterised spectroscopically (^1H, ^{13}C, ^{31}P, ^{11}B (for **3**), MS, and IR). A crystal structure determination of the R_C,R_C,R_P/S_C,S_C,S_P isomer of **1** was obtained. The complexes **1**–**3** were studied in the catalytic polymerisation of ethylene and propylene by activating them with methylalumoxane (MAO) as cocatalyst. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: P–H functionalised phosphinoalkoxide; Zirconocene complex; Heterodinuclear molybdenum phosphine complex; Borane adduct

1. Introduction

While tertiary phosphinoalcohols have been known and employed as ligands in the synthesis of transition metal complexes with catalytic properties for a long time [1], the corresponding secondary P–H functionalised phosphinoalcohols have remained largely unexplored. Only recently has the synthetic potential of primary [2] and secondary [3] phosphinoalcohols in the formation of organic P heterocycles been recognised.

In most transition metal complexes, the tertiary phosphinoalcohol acts as a chelating ligand [1]. Only a small number of heterodinuclear complexes in which a tertiary phosphinoalcohol bridges two different metals (Zr/Rh [4,5], Zr/Ni [6]) are known. Recent advances in early–late bridged transition metal complexes are accredited to the advantageous influence of the supporting ligation of the early transition metal on the catalytic properties of the late transition metal in selective organic transformations [7,8]. This cooperative reactivity stems from the possibility for the electron-poor early transition metal and the electron-rich late transition metal to create an ideal environment for heterolytic bond cleavage of polar substrates. Although many

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early–late transition metal heterobimetallic complexes have been prepared, few of them have shown a truly cooperative synergetic reactivity with organic substrates [9]. The observed reactions were shown to occur at a single metal centre, presumably because the large distance between the metal centres does not allow any synergetic effect. Reactivity is normally found at the late transition metal centre due to coordinative saturation of the early transition metal centre. Nevertheless, some cases have been published in which the early transition metal influences the reactivity of the late transition metal centre [10]. Only in a few reactions has participation of both metal atoms in a reaction with an organic substrate been observed [5,11].

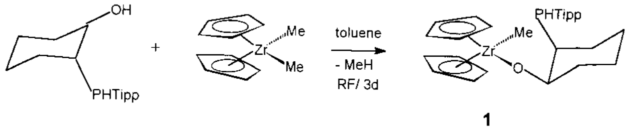
During the last decade major advances have been made in the design and synthesis of well-defined or single-site catalysts for the polymerisation of olefins [12]. The majority of these catalysts are of the metallocene type, although some are known that contain a single cyclopentadienyl ring and, for example, a pendant amido ligand [13,14]. In all the systems, the precatalysts are the dialkyl metallocenes or the corresponding dichlorides with activation by methylalumoxane (MAO), which produces the dialkyl complexes in situ.

We now report the synthesis of the first mono- and heterobimetallic organometallic complexes with a secondary phosphinoalkoxide ligand, [$Cp_2Zr(Me)$(*cyclo*-1-O-2-PH(Tipp)–C_6H_{10})] (**1**) (Tipp = 2,4,6-$Pr^i_3C_6H_2$) and [$Cp_2Zr(Me)$(*cyclo*-1-O-2-PH(Tipp){$Mo(CO)_5$}–C_6H_{10})] (**2**), as well as the borane adduct [$Cp_2Zr(BH_4)$(*cyclo*-1-O-2-PH(Mes)(BH_3)–C_6H_{10})] (**3**) (Mes = 2,4,6-Me_3-C_6H_2). Also addressed in this paper is the possibility of activating zirconocene phosphinoalkoxide complexes with MAO. Moreover, a comparison between complexes in which different phosphinoalkoxide ancillary ligands are attached to a second late transition metal complex (as in **2**) or to a strong Lewis acid (as in **3**) was undertaken to study counteranion effects. In the presence of MAO, complexes **1**–**3** were found to be active catalysts for the polymerisation of α-olefins.

2. Results and discussion

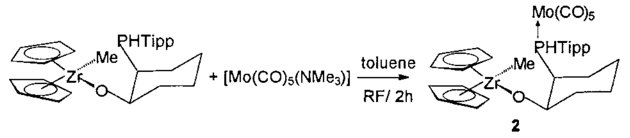
The P–H functionalised phosphinoalcohols 1-PHR-2-OH-*cyclo*-C_6H_{10} (R = Tipp, Mes), which have three chiral centres, were prepared from cyclohexene oxide and LiPHR followed by hydrolytic workup [15]. Due to geometric requirements, only two diastereoisomers are formed (R_C,R_C,S_P/S_C,S_C,R_P) and (R_C,R_C,R_P/S_C,S_C,S_P) in a ratio of 1:1 (for R = Mes) or 2:3 (for R = Tipp) [15]. For the latter, the R_C,R_C,R_P/S_C,S_C,S_P isomer can be obtained in pure form by fractional crystallisation [15].

1-PH(Tipp)-2-OH-*cyclo*-C_6H_{10} (diastereomeric mixture) reacts with [Cp_2ZrMe_2] [16] with elimination of one equivalent of methane to give the mono-substituted product [$Cp_2Zr(Me)$(*cyclo*-1-O-2-PH(Tipp)–C_6H_{10})] (**1**) (Eq. (1)). Even at elevated temperature (boiling toluene), no further elimination of methane is observed.



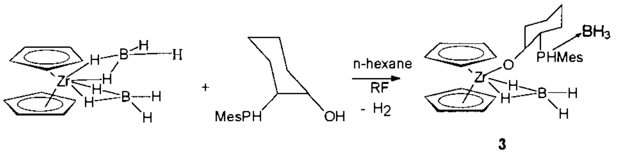
(1)

The phosphino group is not coordinated to zirconium, as is indicated by its ^{31}P-NMR chemical shift, which remains largely unchanged (free ligand: -77.6, d, $^1J_{P-H} = 216.0$ Hz, -89.9 ppm, d, $^1J_{P-H} = 220.0$ Hz [15], **1**: -74.7, d, $^1J_{P-H} = 207.2$ Hz, -90.8, d, $^1J_{P-H} = 222.5$ Hz). The pendant phosphino group can now be employed in the coordination of a second metal. Thus, [$Mo(CO)_5(NMe_3)$] [17] readily reacts with **1** to give the heterodinuclear complex [$Cp_2Zr(Me)$(*cyclo*-1-O-2-PH-(Tipp){$Mo(CO)_5$}–C_6H_{10})] (**2**) (Eq. (2)). While the zirconocene complex is colourless, the dinuclear complex is beige. As expected, the dinuclear complex exhibits a low-field shift in the ^{31}P-NMR spectrum of about 50 ppm and an increase in the P–H coupling constant of 100 Hz (**2**: -43.9, d of d, $^1J_{P-H} = 317.5$ Hz, $^2J_{P-H} = 35.4$ Hz, and -50.7, d of d, $^1J_{P-H} = 318.7$ Hz, $^2J_{P-H} = 22.0$ Hz).



(2)

The borane adduct [$Cp_2Zr(BH_4)$(*cyclo*-1-O-2-PH-(Mes)(BH_3)–C_6H_{10})] (**3**) was obtained from [Cp_2Zr-$(BH_4)_2$] [18,19] and a diastereomeric mixture of 1-PH-(Mes)-2-OH-*cyclo*-C_6H_{10} in boiling hexane (Eq. (3)). The two different boron atoms of the borane and the borato group appear as broad signals at -22.0 (BH_4) and -39.2 ppm (BH_3) in the ^{11}B-NMR spectrum. In the ^{31}P-NMR spectrum, the signal is shifted to -23.4 (d, $^1J_{P-H} = 387.0$ Hz). The diastereomers are not observed due to broadness of the signal.



(3)

2.1. Molecular structure of (R_C,R_C,R_P/S_C,S_C,S_P)-[$Cp_2Zr(Me)$(*cyclo*-1-O-2-PHR–C_6H_{10})] (1)

Single crystals of **1**, suitable for crystal structure determination, were obtained from hexane. The compound crystallises in the monoclinic space group $P2_1/n$ (no. 14) with four formula units in the unit cell. Only one of the two diastereomers (the *rac* isomer with $R_C,R_C,R_P/S_C,S_C,S_P$ configuration) is present (Fig. 1, Table 1). While several zirconocene alkoxide and aryloxide complexes have been reported [7b,20–25], to our knowledge, **1** is only the second structurally characterised zirconocene phosphinoalkoxide complex to date. The other known complex, $[Cp_2Zr(Me)(OCPh_2PH\text{-}Mes)]$, was obtained from the reaction of benzophenone with $[Cp_2Zr(Me)Cl]$ and LiPHMes [26].

In **1**, the Zr atom is coordinated in a distorted tetrahedral fashion by two Cp ligands, one methyl group and a phosphinoalkoxide ligand. The structural data of the Zr–O–C fragment are comparable to those of related zirconocene alkoxide complexes (Table 2). In all complexes, the short Zr–O bond lengths and large Zr–O–C bond angles indicate a partial double bond, ascribable to π donation from the oxygen atom to the empty $1a_1$ orbital of Zr [27].

The overall structure of the phosphinoalkoxide ligand is comparable to that of the free ligand [15]. Both the O and P substituents occupy equatorial positions of the cyclohexyl ring.

2.2. *Catalytic polymerisation studies*

The catalytic polymerisation of ethylene and propylene was studied with the catalyst precursors **1**–**3**. Cationic catalysts were generated in toluene by the reaction of the precursors with an excess of MAO. The polymerisations were carried out under strictly anaerobic/anhydrous conditions. The reactions were quenched after measured time intervals with methanol/HCl solutions prior to polymer collection, washing with hexane and acetone and drying at 70°C. In the case of ethylene, high-density polyethylene was obtained, and propylene was converted to atactic polypropylene.

Table 3 lists the ethylene and propylene polymerisation results obtained with the catalytic systems **1**–**3**/MAO. For all the complexes, the activity towards propylene is higher than towards ethylene, although in comparison with the simple metallocenes, the activity in the latter case is an order of magnitude higher. The activity follows the order $\mathbf{1} > \mathbf{2} > \mathbf{3}$. Hence, it can be expected that MAO will cleave off the phosphinoalkoxide ligand of **1** and **2** to produce the cationic complex $[Cp_2ZrMe]^+$, whereby the counteranion is responsible for the difference in activity. A similar result was obtained for other bimetallic early–late transition metal complexes in the polymerisation of ethylene and propylene [28]. To corroborate these results, we performed a comparitive study on the polymerisation of ethylene by using complex **1** with MAO and its precursor $[Cp_2ZrMe_2]$ with MAO and an equimolar amount (based on the complex) of the free ligand 1-PH(Tipp)-2-OH-*cyclo*-C_6H_{10}. The activity of the latter system is 6.73×10^3 g mol^{-1} h^{-1}, that is, two orders of magnitudes smaller than that of complex **1** with MAO. This result strongly indicates that the phosphinoalcoholate moiety in conjunction with MAO acts as a better counterion for the cationic complex $[Cp_2ZrMe]^+$ than the system Me/MAO. For complex **3** to be active in the polymerisation of α-olefins, a cationic metal–carbon bond must be formed. This process can plausibly occur by the replacement of the borate ligand with a methyl group by MAO, similar to the reaction of dichlorozir-

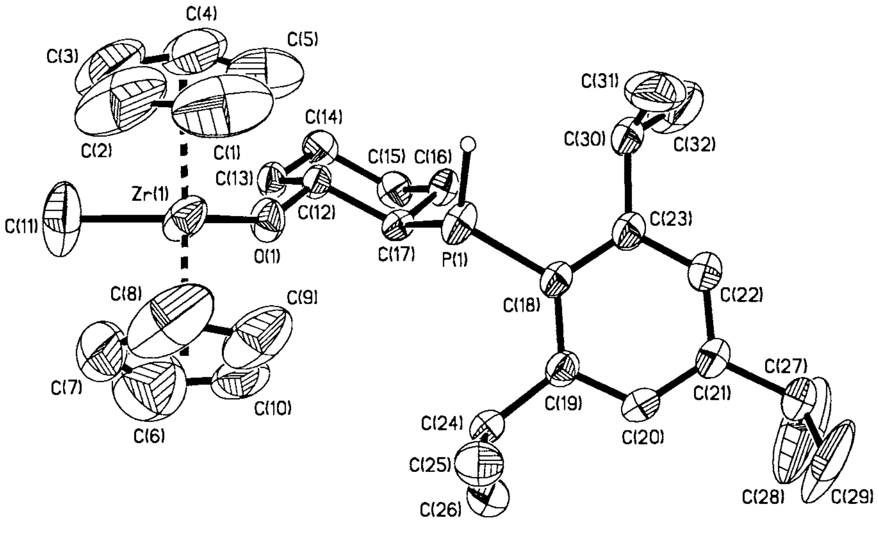


Fig. 1. Molecular structure of **1** (ORTEP, 50% probability, SHELXTL PLUS; XP) [30]. Hydrogen atoms other than P–H are omitted for clarity. Only one enantiomer with R_C,R_C,R_P configuration is shown.

Table 1
Selected bond lengths (Å) and angles (°) in **1**

Bond lengths			
Zr(1)–O(1)	1.938(3)	Zr(1)–C(11)	2.294(6)
P(1)–C(18)	1.843(4)	P(1)–C(17)	1.866(4)
P(1)–H(1P)	1.39(5)	O(1)–C(12)	1.402(5)
C(12)–C(13)	1.520(6)	C(12)–C(17)	1.528(5)
C(13)–C(14)	1.515(6)	C(14)–C(15)	1.510(6)
C(15)–C(16)	1.536(6)	C(16)–C(17)	1.529(6)
C(18)–C(19)	1.414(6)	C(18)–C(23)	1.416(6)
C(19)–C(20)	1.388(6)	C(19)–C(24)	1.524(6)
C(20)–C(21)	1.383(6)	C(21)–C(22)	1.382(6)
C(21)–C(27)	1.523(6)	C(22)–C(23)	1.393(6)
C(23)–C(30)	1.522(6)	C(24)–C(26)	1.518(7)
C(24)–C(25)	1.528(7)	C(27)–C(28)	1.443(10)
C(27)–C(29)	1.446(9)	C(30)–C(32)	1.505(9)
C(30)–C(31)	1.538(9)		
C(Cp)–C(Cp)	1.36(1)–1.45(1)		
Zr–C(Cp)	2.492(7)–2.549(7)		
Bond angles			
O(1)–Zr(1)–C(11)	97.3(2)	C(18)–P(1)–C(17)	105.3(2)
C(18)–P(1)–H(1P)	116.0(2)	C(17)–P(1)–H(1P)	118(2)
C(12)–O(1)–Zr(1)	152.8(3)	O(1)–C(12)–C(13)	110.0(3)
O(1)–C(12)–C(17)	110.9(3)	C(13)–C(12)–C(17)	111.1(3)
C(14)–C(13)–C(12)	113.1(4)	C(15)–C(14)–C(13)	111.1(4)
C(14)–C(15)–C(16)	110.4(4)	C(17)–C(16)–C(15)	110.6(4)
C(12)–C(17)–C(16)	110.6(3)	C(12)–C(17)–P(1)	108.9(3)
C(16)–C(17)–P(1)	112.0(3)	C(19)–C(18)–C(23)	119.0(3)
C(19)–C(18)–P(1)	122.5(3)	C(23)–C(18)–P(1)	118.2(3)
C(20)–C(19)–C(18)	118.7(4)	C(20)–C(19)–C(24)	118.2(4)
C(18)–C(19)–C(24)	123.0(3)	C(21)–C(20)–C(19)	123.0(4)
C(22)–C(21)–C(20)	117.5(4)	C(22)–C(21)–C(27)	120.1(4)
C(20)–C(21)–C(27)	122.3(4)	C(21)–C(22)–C(23)	122.4(4)
C(22)–C(23)–C(18)	119.1(4)	C(22)–C(23)–C(30)	118.2(4)
C(18)–C(23)–C(30)	122.7(4)	C(26)–C(24)–C(19)	113.5(4)
C(26)–C(24)–C(25)	110.2(5)	C(19)–C(24)–C(25)	110.7(4)
C(28)–C(27)–C(29)	112.0(7)	C(28)–C(27)–C(21)	112.1(5)
C(29)–C(27)–C(21)	114.3(5)	C(32)–C(30)–C(23)	113.1(5)
C(32)–C(30)–C(31)	112.8(6)	C(23)–C(30)–C(31)	110.4(5)
C(Cp)–C(Cp)–C(Cp)	105.7(8)–110.1(8)		

conocenes with MAO, and concomitant abstraction of the phosphinoalcohol moiety to form the cationic complex. Corroboration for the formation of a cationic zirconocene methyl complex was provided by the ^{13}C-NMR spectrum of the mixture of complex **3** with MAO, which shows the same methyl signal at 40.9 ppm as is found for [Cp_2ZrMe_2]/MAO and for the cation of $[Cp_2ZrMe]^+[MeB(C_6F_5)_3]^-$ [29]. Hence, borohydride complexes are also expected to be active precursors for the polymerisation of α-olefins by metallocene complexes. To study the effect of the counterion on the catalytic activity, we performed the polymerisation of ethylene, using zirconocene dichloride, MAO, and one equivalent of the free phosphinoalcohol. The activity for ethylene polymerisation, under the same catalytic conditions, is 3.5×10^5 g mol^{-1} h^{-1}, which is similar to the activity of complexes **1** and **2**. This result suggests that the anionic effect of the Cl/MAO counterion is similar to that of the phosphinoalcohol/MAO system.

3. Experimental

All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. The NMR spectra were recorded at 25°C in C_6D_6 with an Avance DRX 400 spectrometer (Bruker), ^{1}H-NMR: internal standard solvent (benzene), external standard TMS; ^{13}C-NMR: external standard TMS, internal standard solvent; ^{31}P-NMR: external standard 85% H_3PO_4; ^{11}B-NMR: external standard $BF_3{\cdot}Et_2O$. The IR spectra were recorded on a FTIR spectrometer Perkin–Elmer System 2000 in the range 350–4000 cm^{-1}. The mass spectra were recorded with an MAT-212 (Finnigan), EI MS, 70 eV. The melting points were determined in sealed capillaries under argon and are uncorrected.

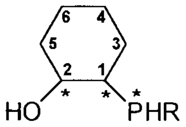
1-PHR-2-OH-*cyclo*-C_6H_{10} (R = Tipp, Mes) [15], [Cp_2ZrMe_2] [16], [$Mo(CO)_5(NMe_3)$] [17], and [$Cp_2Zr(BH_4)_2$] [18] were prepared according to literature procedures.

3.1. [$Cp_2Zr(Me)$(*cyclo*-1-O-2-PH(Tipp)–C_6H_{10})] (1)

A total of 1.5 g (6 mmol) [Cp_2ZrMe_2] was dissolved in 50 ml of toluene and 2.0 g (6 mmol) of 1-PH(Tipp)-2-OH-*cyclo*-C_6H_{10} was added. Evolution of gas (methane) was observed. The mixture was stirred at room temperature (r.t.) for 3 h. Then the solvent was removed in vacuo, the resulting yellow oil was dissolved in 25 ml of pentane, and the solution cooled to − 20°C. After several days, **1** was obtained as a colourless microcrystalline solid: 2.1 g (61.5%); m.p. 107–110°C dec.

^{1}H-NMR (C_6D_6): $\delta = 7.18$ (s, 4H, 2 isomers, *m*-H in Tipp), 5.91 (s, 5H, 1 isomer, Cp), 5.90 (s, 5H, 1 isomer,Cp), 5.882 (s, 5H, 1 isomer, Cp), 5.876 (s, 5H, 1 isomer, Cp), 4.74 (d of d, 1H, 1 isomer, PH, $^1J_{P-H} = 222.5$ Hz, $^3J_{H-H} = 5.6$ Hz), 4.24 (d of d, 1H, 1 isomer, PH, $^1J_{P-H} = 207.5$ Hz, $^3J_{H-H} = 9.5$ Hz), 4.12 (sept, 2H, 1 isomer, $^3J_{H-H} = 5.9$ Hz, *o*-C*H*(CH_3)$_2$), 3.76 (sept, 2H, 1 isomer, $^3J_{H-H} = 6.4$ Hz, *o*-C*H*(CH_3)$_2$), 3.62 (m, 2H, 2 isomers, O-C*H*, Cy), 2.79 (sept, 2H, 2 isomers, $^3J_{H-H} =$ 6.9 Hz, *p*-C*H*(CH_3)$_2$), 2.1–0.9 (m, 18H, 2 isomers, Cy), 1.40 (d, 12H, 1 isomer, *o*-CH(C*H*$_3$)$_2$), 1.31 (d, 12H, 1 isomer, *o*-CH(C*H*$_3$)$_2$), 1.23 (d, 12H, 2 isomers, *p*-CH(C*H*$_3$)$_2$), 0.41 (s, 6H, 2 isomers, Zr-CH_3).

Cyclohexyl numbering scheme:



$^{13}C\{H\}$-NMR (C_6D_6): $\delta = 155.54$ (d, 2C, 1 isomer, *o*-C in Tipp, $^2J_{P-C} = 10.9$ Hz), 153.29 (d, 2C, 1 isomer, *o*-C in Tipp, $^2J_{P-C} = 10.9$ Hz), 150.85 (s, 1C, 1 isomer, *p*-C in Tipp), 149.76 (s, 1C, 1 isomer, *p*-C in Tipp), 133.55 (d, 2C, 2 isomers, *ipso*-C in Tipp, $^1J_{P-C} = 58.4$ Hz), 127.73 (s, 2C, 1 isomer, *m*-C in Tipp), 127.58 (s, 2C, 1 isomer, *m*-C in Tipp), 111.44 (s, 5C, 1 isomer, Cp), 111.25 (s, 5C, 1 isomer, Cp), 111.18 (s, 5C, 1 isomer, Cp), 111.15 (s, 5C, 1 isomer, Cp), 85.83 (d, 1C, 1 isomer, O–CH, $^2J_{P-C} = 13.5$ Hz), 84.62 (d, 1C, 1 isomer, O–CH, $^2J_{P-C} = 10.9$ Hz), 45.32 (d, 1C, 1 isomer, P–CH, $^1J_{P-C} = 13.0$ Hz), 45.93 (d, 1C, 1 isomer, P–CH, $^1J_{P-C} = 11.3$ Hz), 38.80 (d, 1C, 1 isomer, C5 in Cy, $^3J_{P-C} = 7.6$ Hz), 38.38 (s, 1C, 1 isomer, C5 in Cy), 35.43 (s, 1C, 1 isomer, *p*-CH($CH_3)_2$), 35.37 (s, 1C, 1 isomer, *p*-CH($CH_3)_2$), 33.97 (d, 2C, 1 isomer, *o*-CH($CH_3)_2$, $^3J_{P-C} = 12.3$ Hz), 33.63 (d, 2C, 1 isomer, *o*-CH($CH_3)_2$, $^3J_{P-C} = 15.4$ Hz), 29.35 (d, 2C, 2 isomers, C3 in Cy, $^2J_{P-C} = 14.1$ Hz), 27.06 (d, 2C, 2 isomers, C4 in Cy, $^3J_{P-C} = 9.5$ Hz), 25.96 (s, 4C, 1 isomer, *o*-CH($CH_3)_2$), 25.77 (s, 4C, 1 isomer, *o*-CH($CH_3)_2$), 25.50 (s, 4C, 2 isomers, *p*-CH($CH_3)_2$), 25.00 (s, 1C, 1 isomer, C6 in Cy), 24.83 (s, 1C, 1 isomer, C6 in Cy), 20.41 (s, 1C, 1 isomer, Zr–CH_3), 19.93 (s, 1C, 1 isomer, Zr–CH_3). ^{31}P-NMR (C_6D_6): $\delta = -74.7$ (d, $^1J_{P-H} = 207.2$ Hz), -90.8 (d, $^1J_{P-H} = 222.5$ Hz). EI MS: *m/z* 570 (3%, M^+), 555 (57%, M^+–Me), 235 (35%, $PHTipp^+$), and fragmentation thereof. IR (KBr): ν (cm^{-1}): 2349 m (νPH).

Anal. Calc. for $C_{32}H_{47}OPZr$ (569.89), C 67.4, H 8.3, P 5.4. Found: C 65.4, 8.4, P 5.1%.

Recrystallisation from hexane yielded colourless rhombohedral platelets of **1** consisting of both diastereomers as shown by ^{31}P-NMR spectroscopy.

*3.2. [Cp$_2$Zr(Me)(cyclo-1-O-2-PH(Tipp)-{Mo(CO)$_5$}–C$_6$H$_{10}$)] (**2**)*

A total of 0.60 g of **1** (1.05 mmol) was dissolved in 20 ml of toluene, and 0.31 g of $[Mo(CO)_5(NMe_3)]$ (1.05 mmol) was added. Then the mixture was heated to 100°C for 2 h. After cooling to r.t., the solvent was removed, and the beige residue washed with 10 ml of pentane. The beige solid was redissolved in 50 ml of hexane, and the solution was cooled to −20°C. **2** was obtained as a beige solid: 0.65 g (77%); m.p. 89°C dec.

^1H-NMR (C_6D_6): $\delta = 7.07$ (s, 2H, 1 isomer, *m*-H in Tipp), 7.04 (s, 2H, 1 isomer, *m*-H in Tipp), 6.12 (d of d, 1H, 1 isomer, PH, $^1J_{P-H} = 318.8$ Hz, $^3J_{H-H} = 11.8$ Hz), 6.05 (d of d, 1H, 1 isomer, PH, $^1J_{P-H} = 317.6$ Hz, $^3J_{H-H} = 11.0$ Hz), 5.86 (s, 5H, 1 isomer, Cp), 5.80 (s, 5H, 1 isomer, Cp), 5.66 (s, 5H, 1 isomer, Cp), 5.49 (s, 5H, 1 isomer, Cp), 3.63 (m, 2H, 2 isomers, O–CH, Cy), 3.49 (m, 2H, 1 isomer, *o*-CH($CH_3)_2$), 3.35 (m, 2H, 1 isomer, *o*-CH($CH_3)_2$), 2.62 (m, 2H, 2 isomers, *p*-CH($CH_3)_2$), 2.05–0.85 (m, 18H, 2 isomers, Cy), 1.40 (d, 6H, 1 isomer, *o*-CH($CH_3)_2$), 1.36 (d, 6H, 1 isomer, *o*-CH($CH_3)_2$), 1.32 (d, 6H, 1 isomer, *p*-CH($CH_3)_2$), 1.28 (d, 6H, 1 isomer, *p*-CH($CH_3)_2$), 1.09 (d, 6H, 1 isomer, *o*-CH($CH_3)_2$), 1.06 (d, 6H, 1 isomer, *o*-CH($CH_3)_2$), 0.17 (s, 6H, 2 isomers, Zr–CH_3). $^{13}C\{H\}$-NMR (C_6D_6): $\delta = 206.67$ (d, 5C, 1 isomer, $^2J_{P-C} = 8.6$ Hz, CO),

Table 2
Comparison of selected bond lengths and angles of **1** with those of related complexes

Compound	Zr–O (Å)	Zr–O–C (°)	Ref.
$[Cp_2ZrBz\{O\text{-}2,4\text{-}Me_2\text{-}6\text{-}(\alpha\text{-methylcyclohexyl})C_6H_2\}]$	1.981(6)	165.3(5)	[20]
$[Cp_2ZrCl\{O\text{-}2,6\text{-}Bu^t_2\text{-}4\text{-}MeC_6H_2\}]$	1.98(2)	150(1)	[21]
$[Cp_2Zr(NMe_2)\{O\text{-}2,6\text{-}Bu^t_2C_6H_3\}]$	2.056(1)	142.7(1)	[21]
$[Cp_2Zr(OEt)\{2\text{-naphthyl-}1\text{-}B(OEt)_2\}]$	1.916(5)	160.2(6)	[22]
$[Cp_2ZrCl\{OCMe_2CH_2CH_2Zr(Cl)Cp_2\}]$	1.921(4)	165.9(4)	[23]
E-$[Cp_2ZrCl\{OC(PPh_2){=}CHMe\}]$	1.955(5)	160.5(5)	[24]
$[Cp_2Zr\{OCH_2C_6H_5Cr(CO)_3\}_2]$	1.956(2)	155.9(2)	[25]
	1.948(2)	157.9(3)	
$[Cp_2Zr(Me)(OCPh_2PHMes)]$	1.926(9)	167.7(9)	[26]
1	1.938(3)	152.8(3)	This work

Table 3
Ethylene and propylene polymerisation results obtained with the catalytic systems **1**–**3**/MAO

Complex	MAO/complex ratio	Activity for polyethylene (g mol^{-1} h^{-1})	Activity for polypropylene (g mol^{-1} h^{-1})
1	1000	5.0×10^5	6.9×10^5
2	1000	2.5×10^5	5.8×10^5
3	1000	6.9×10^4	1.2×10^5

206.54 (d, 5C, 1 isomer, $^2J_{P-C} = 8.5$ Hz, CO), 152.22 (d, 2C, 2 isomers, *p*-C in Tipp, $^4J_{P-C} = 13.2$ Hz,), 151.44 (d, 4C, 2 isomers, *o*-C in Tipp, $^2J_{P-C} = 16.7$ Hz), 126.34 (d, 1C, 1 isomer, *ipso*-C in Tipp, $^1J_{P-C} = 35.3$ Hz), 125.76 (d, 1C, 1 isomer, *ipso*-C in Tipp, $^1J_{P-C} = 34.9$ Hz), 123.72 (d, 2C, 1 isomer, *m*-C in Tipp, $^3J_{P-C} = 7.2$ Hz), 122.83, (d, 2C, 1 isomer, *m*-C in Tipp, $^3J_{P-C} = 5.1$ Hz), 111.18 (s, 5C, 1 isomer, Cp), 111.02 (s, 5C, 1 isomer, Cp), 110.92 (s, 5C, 1 isomer, Cp), 110.61 (s, 5C, 1 isomer, Cp), 78.49 (s, 1C, 1 isomer, O–CH), 78.44 (s, 1C, 1 isomer, O–CH), 39.60 (d, 1C, 1 isomer, P–CH, $^1J_{P-C} = 13.1$ Hz), 39.05 (d, 1C, 1 isomer, P–CH, $^1J_{P-C} = 12.8$ Hz), 35.40 (s, 1C, 1 isomer, *p*-*C*H(CH_3)$_2$), 35.30 (s, 1C, 1 isomer, *p*-*C*H(CH_3)$_2$), 34.82 (s, 2C, 1 isomer, *o*-*C*H(CH_3)$_2$), 34.74 (s, 2C, 1 isomer, *o*-*C*H(CH_3)$_2$), 34.11 (d, 1C, 1 isomer, C3 in Cy, $^2J_{P-C} = 11.9$ Hz), 34.03 (d, 1C, 1 isomer, C3 in Cy, $^2J_{P-C} = 12.5$ Hz), 33.09 (d, 1C, 1 isomer, C4 in Cy, $^3J_{P-C} = 3.7$ Hz), 32.89 (d, 1C, 1 isomer, C4 in Cy, $^3J_{P-C} = 4.9$ Hz), 30.80 (s, 1C, 1 isomer, C5 in Cy), 30.61 (s, 1C, 1 isomer, C5 in Cy), 26.06 (s, 1C, 1 isomer, C6 in Cy), 25.97 (s, 1C, 1 isomer, C6 in Cy), 25.91 (s, 1C, 1 isomer, *o*-CH(*C*H_3)$_2$), 25.75 (s, 1C, 1 isomer, *o*-CH(*C*H_3)$_2$), 25.67 (s, 1C, 1 isomer, *o*-CH(*C*H_3)$_2$), 25.60 (s, 1C, 1 isomer, *o*-CH(*C*H_3)$_2$), 24.75 (s, 2C, 1 isomer, *p*-CH(*C*H_3)$_2$), 24.65 (s, 2C, 1 isomer, *p*-CH(*C*H_3)$_2$), 24.63 (s, 1C, 1 isomer, *o*-CH(*C*H_3)$_2$), 24.37 (s, 1C, 1 isomer, *o*-CH(*C*H_3)$_2$), 24.21 (s, 1C, 1 isomer, *o*-CH(*C*H_3)$_2$), 24.17 (s, 1C, 1 isomer, *o*-CH(*C*H_3)$_2$), 21.01 (s, 1C, 1 isomer, Zr–CH_3), 19.54 (s, 1C, 1 isomer, Zr–CH_3). ^{31}P-NMR (C_6D_6): $\delta = -43.9$ (d of d, $^1J_{P-H} = 317.5$ Hz, $^2J_{P-H} = 35.4$ Hz), -50.7 (d of d, $^1J_{P-H} = 318.7$ Hz, $^2J_{P-H} = 22.0$ Hz). EI MS: *m*/*z* 806 (3%, M^+), 235 (5%, $PHTipp^+$), and fragmentation thereof. IR (KBr): ν (cm^{-1}): 2349 m (νPH), 2070 s, 1986 s, 1943 vs (νCO).

Anal. Calc. for $C_{37}H_{47}MoO_6PZr$ (806.31), C 55.1, H 5.8, P 3.8. Found: C 54.8, H 5.6, P 3.2%.

3.3. [$Cp_2Zr(BH_4)$(cyclo-1-O-2-PH(Mes)(BH_3)–C_6H_{10})] (3)

A total of 1.4 g (5.6 mmol) [$Cp_2Zr(BH_4)_2$] was suspended in 50 ml of hexane, and 1.4 g (5.6 mmol) of 1-PH(Mes)-2-OH-*cyclo*-C_6H_{10} was added. As no reaction was observed at r.t. (no evolution of gas), the mixture was heated to reflux for 12 h, during which the solid dissolved and the solution turned pale red. After cooling to r.t., the solvent was removed, and the red residue was extracted with Et_2O. After several days, **1** was obtained as a pale-red solid: 1.5 g (55%); m.p. 148°C.

^{1}H-NMR (C_6D_6): $\delta = 6.64$ (s, 4H, 2 isomers, *m*-H in Mes), 6.00 (s, 10H, 2 isomers, Cp), 5.94 (s, 10H, 2 isomers, Cp), 4.13 (m, 2H, 2 isomers, O–CH, Cy), 4.06 (d, 2H, 2 isomers, PH, $^1J_{P-H} = 387.3$ Hz), 2.55 (s, 12H, 2 isomers, *o*-CH_3), 2.00 (s, 6H, 2 isomers, *p*-CH_3), 1.81–0.69 (m, 32H, 2 isomers, Cy, BH_3 and BH_4). ^{13}C{H}-NMR (C_6D_6): $\delta = 144.45$ (d, 4C, 2 isomers, *o*-C in Mes, $^2J_{P-C} = 7.5$ Hz), 141.83 (d, 2C, 2 isomers, *p*-C in Mes, $^4J_{P-C} = 3.9$ Hz), 131.16 (d, 4C, 2 isomers, *m*-C in Mes, $^3J_{P-C} = 8.0$ Hz), 121.32 (d, 2C, 2 isomers, *ipso*-C, $^1J_{P-C} = 48.8$ Hz), 113.28 (s, 5C, 1 isomer, Cp), 113.22 (s, 5C, 1 isomer, Cp), 113.13 (s, 5C, 1 isomer, Cp), 113.06 (s, 5C, 1 isomer, Cp), 81.81 (s, 2C, 2 isomers, O–CH), 44.54 (d, 2C, 2 isomers, P–CH, $^1J_{P-C} = 32.7$ Hz), 38.22 (d, 2C, 2 isomers, C3 in Cy, $^2J_{P-C} = 8.2$ Hz), 26.29 (d, 2C, 2 isomers, C5 in Cy, $^3J_{P-C} = 12.0$ Hz), 25.57 (s, 2C, 2 isomers, C4 in Cy), 25.41 (s, 2C, 2 isomers, C6 in Cy), 24.01 (s, 2C, 2 isomers, *o*-Me in Mes), 23.96 (s, 2C, 2 isomers, *o*-Me in Mes), 21.59 (s, 2C, 2 isomers, *p*-Me in Mes). ^{31}P-NMR (C_6D_6): $\delta = -23.4$ (d, $^1J_{P-H} = 387.0$ Hz). ^{11}B-NMR (C_6D_6): $\delta = -22.0$ (br, s, BH_4), -39.2 (br, s, BH_3).

EI MS: *m*/*z* 499 (3%, M^+), 470 (7%, M^+–(B_2H_6)), 237 (27%, $Cp_2Zr(BH_4)^+$), and fragmentation thereof. IR (KBr): ν (cm^{-1}): 2369 s (νPH).

Anal. Calc. for $C_{25}H_{39}B_2OPZr$ (499.39), C 60.1, H 7.9, P 6.2. Found: C 60.4, H 7.8, P 5.8%.

3.4. Polymerisation experiments

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high-vacuum (10^{-5} torr) line, or in a nitrogen-filled Vacuum Atmospheres glove box with a medium capacity recirculator (1–2 ppm O_2). Argon, ethylene, propylene and nitrogen gases were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. All solvents for vacuum line manipulations were stored in vacuo over Na–K alloy in resealable bulbs.

The polymerisation experiments were conducted in a 100 ml flamed round-bottom reaction flask attached to a high-vacuum line. In a typical experiment, 4.0 mg of **1** and 500 mg of MAO (Zr:Al = 1:1000) were charged to the flask containing a magnetic stir bar. The reaction vessel was connected to a high-vacuum line, pumped down and back-filled for three times with argon. Then the flask was reevacuated and a measured quantity of toluene (40 ml) was vacuum transferred into the reaction flask from Na–K. Then gaseous propylene was condensed into the vessel through a gas purification column. The flask was warmed to r.t., and the pressure was continuously measured by means of a manometer. Rapid stirring of the solution was initiated, and after a measured time interval (2 h), polymerisation was quenched by releasing the excess pressure of propylene and immediately injecting a methanol–HCl mixture. The polymer product was collected by filtration, washed with hexane and acetone and dried under vacuum for several hours.

3.5. *X-ray crystal structure determination for* ***1***

Data (λ(Mo–K$_\alpha$) = 0.71073 Å) were collected on a Siemens CCD (SMART). All observed reflections were used for determination of the unit cell parameters. The structure was solved by direct methods (SHELXTL PLUS [30]) and subsequent difference Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL PLUS [30]). Zr, C, P and O atoms anisotropic, H atoms refined in fixed positions. Empirical absorption correction with SADABS [31]

3.6. *Crystal data for* ***1***

$C_{32}H_{47}OPZr$, $M = 569.89$, colourless crystals, $0.30 \times 0.20 \times 0.10$ mm, monoclinic, space group $P2_1/n$ (no. 14), $T = 213(2)$ K, $a = 8.837(1)$, $b = 10.846(2)$, $c = 31.997(5)$ Å, $\beta = 93.05(1)°$, $V = 3062.4(9)$ Å^3, $Z = 4$, $D_{calc} = 1.236$ Mg m^{-3}, $F(000) = 1208$, μ(Mo–K$_\alpha$) = 0.432 mm^{-1}, 13 209 reflections collected with $2.0 < \Theta < 27.5°$; of these, 6180 were independent [$R_{int} = 0.0390$]; 399 parameters, refinements converge to $R_1 = 0.0597$, $wR_2 = 0.1336$ (for reflections with $I > 2\sigma(I)$), $R_1 = 0.1034$, $wR_2 = 0.1580$ (all data).

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 133347 (**1**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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