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Formation of elastomeric polypropylene promoted by the dynamic complexes $[TiCl_2\{N(PPh_2)_2\}_2]$ and $[Zr(NPhPPh_2)_4]$☆

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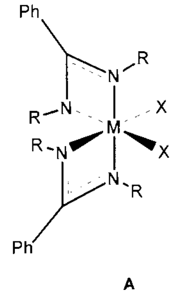
Abstract

The homoleptic phosphinoamide complex $[Zr(NPhPPh_2)_4]$ (**1**) and the bisamido complex $[TiCl_2\{N(PPh_2)_2\}_2]$ (**2**) were prepared from $ZrCl_4$ and four equivalents of $LiNPhPPh_2$ and from $TiCl_4$ and one equivalent of $[Li(THF)N(PPh_2)_2]_2$. In the solid state, the four $NPhPPh_2$ ligands in **1** exhibit η^2 coordination. The ZrN_4P_4 fragment is highly symmetrical and almost of D_2 symmetry. Hence, the complex is chiral, and the two enantiomers cocrystallize in the asymmetric unit. In solution, **1** exhibits signals for the six-coordinate complex $[Zr(\eta^2\text{-}NPhPPh_2)_2(\eta^1\text{-}NPhPPh_2)_2]$. In the presence of methylalumoxane (MAO), **1** and **2** are active catalysts for the formation of high-molecular-weight elastomeric polypropylene. The formation of elastomeric polypropylene is a consequence of an epimerization mechanism of the last-inserted monomer, indicating no detachment of the growing polymer chain from the metal center during this process. Fractionation studies of all the elastomeric polymers show no atactic fractions. As corroboration for this mechanism, we have shown that these complexes are active catalysts for the isomerization and oligomerization of 1-octene, as well as for the rapid isomerization of allylbenzene to *trans*-methylstyrene. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Homoleptic zirconium phosphinoamide complex; Titanium bisamido dichloride complex; Molecular structure; Polymerisation of propylene

1. Introduction

Major advances have been made during the last decade in the design and synthesis of ‘well-defined’ and ‘single-site’ catalysts for the polymerization of olefins [1–3]. The majority of these catalysts belong to the metallocene ensemble, although homogeneous and new heterogeneous complexes that contain one cyclopentadienyl ring and (for example) a pendant amido ligand are also well known and have been of major interest [4–6]. However, recently complexes containing chelating ancillary ligands, such as dialkoxides, diamides, or benzamidines [7–13], have received attention as potential Ziegler–Natta catalysts. We and others have investigated α-olefin polymerization with bis(benzamidinate) dichloride or dialkyl complexes of Group 4 metals (A) as catalysts, which are obtained as a racemic mixture of *cis* octahedral complexes with C_2 symmetry [14–16]. When activated with methylalumoxane (MAO) or perfluoroborane compounds, these complexes were found to be active catalyst precursors for the polymerization of ethylene, propylene, 1-hexene and 2,5-hexadiene [12].



A

(X = Cl, alkyl; R = Pr^i, Bu^t, $SiMe_3$)

☆ These results have been presented in part at the XVIII International Conference on Organometallic Chemistry, Munich, 16–22 August 1998; E. Hey-Hawkins et al., Book of Abstracts 1, AO 32.

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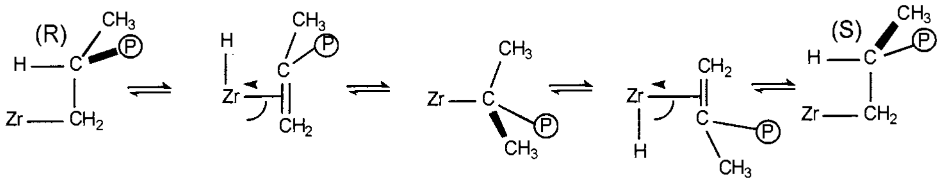


Scheme 1.

In general, the tacticity of the polymers varies predictably with the structure of the metallocene catalysts. Complexes with C_2 or C_1 symmetry are expected to produce isotactic polyolefins, whereas those with C_{2v} symmetry generate atactic polymers [1–3,17]. However, when the polymerization of propylene with **A** is carried out at atmospheric pressure, atactic polypropylene is formed as an oil, instead of the expected isotactic polymer [10,11]. The formation of atactic polypropylene can be rationalized by an intramolecular epimerization reaction of the growing polypropylene chain (P) at the last-inserted monomer unit that is faster than the stereoregular insertion of propylene (Scheme 1) [18–21].

We recently showed that the expected isotactic polypropylene is formed (*mmmm* > 99.5%; m.p. = 153°C) when the polymerization is carried out at high concentration of monomer (i.e. in liquid propylene). Apparently, a high propylene concentration allows faster insertion of the monomer unit and suppresses the epimerization reaction almost completely [22]. These results corroborate the proposed epimerization mechanism [23].

A conceptual question is whether simple octahedral or even tetrahedral complexes that have a dynamic Lewis-basic pendant group that can donate an electron lone pair to the highly electrophilic metal center are suitable for the preparation of a unique type of polymer. Thus, as shown in Scheme 2, a dynamic equilibrium occurs between the tetrahedal and octahedral configurations, whereby only a *cis*-octahedral complex can induce the polymerization of an α-olefin, such as propylene, allowing the production of an elastomer (X = halide, E = a donor group with an electron lone pair, R = C, N, P or other anionic bridging group).

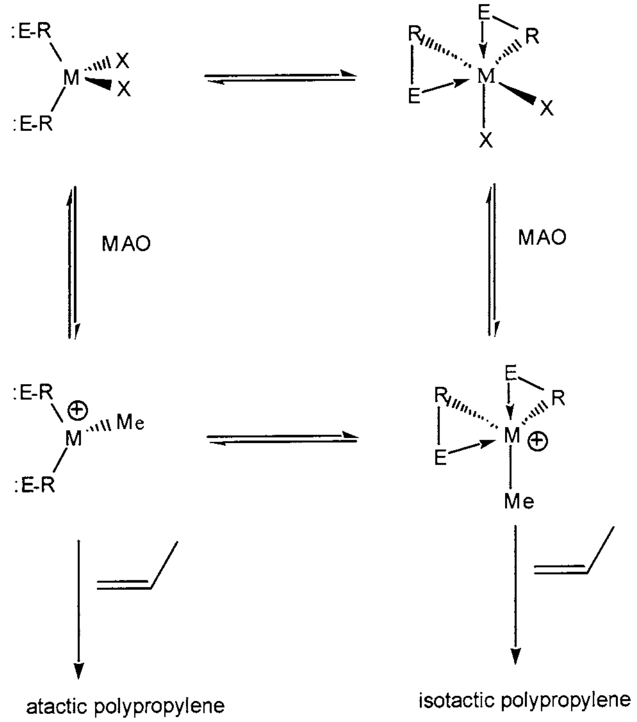
In these types of dynamic processes, a plausible *trans* isomer can be obtained, although it will have no catalytic activity [1–3]. These isomers are unable to perform the insertion of an α-olefin because the incoming monomer unit is *trans* to the growing alkyl chain [7–9]. Here we present the synthesis of two early transition metal complexes that contain pendant donor groups: the homoleptic phosphinoamide complex [Zr(NPhPPh$_2$)$_4$] (**1**) and the bisamido complex [TiCl$_2${N(PPh$_2$)$_2$}$_2$] (**2**). In the presence of methylalumoxane (MAO), these complexes are active catalysts for the formation of elastomeric polypropylene [22–25]. To our knowledge, this is the first example of the rational synthesis of an elastomeric polymer by using octahedral early transition metal complexes.

2. Results and discussion

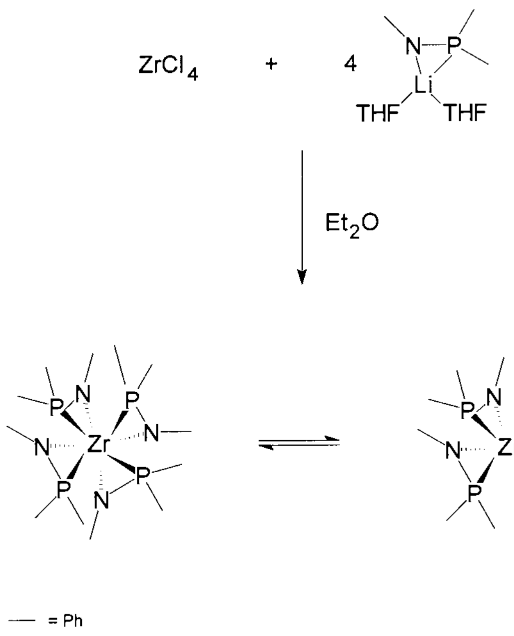
2.1. Synthesis and spectroscopic properties of *1* and *2*

The phosphinoamines Ph$_2$PN(H)Ph [26] and Ph$_2$PN(H)PPh$_2$ [27] are readily deprotonated by BuLi to give LiNPhPPh$_2$ [28] and LiN(PPh$_2$)$_2$ [29], respectively. Two mesomeric structures can be formulated for these anions in which the negative charge is localized at the N (phosphinoamide) or P atom (iminophosphide) (R = Ph, PPh$_2$). According to theoretical calculations [30], the phosphinoamide structure is dominant.

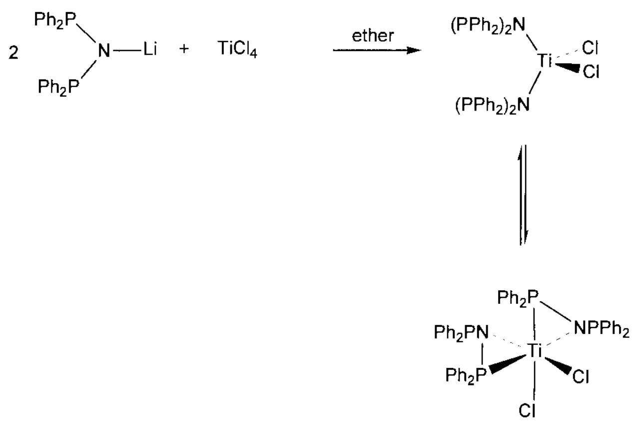
$$Ph_2P\text{-}\overline{N}\text{-}R \longleftrightarrow Ph_2\overline{P}\text{=}N\text{-}R$$



Scheme 2.



Scheme 3.



2

Scheme 4.

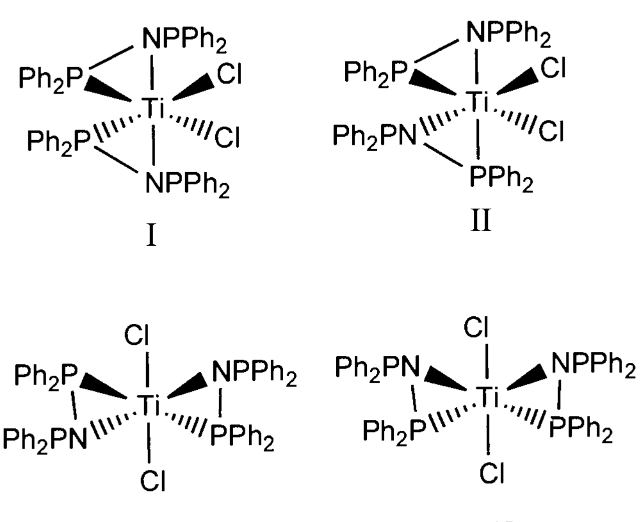
When $ZrCl_4$ is treated with four equivalents of $LiNPhPPh_2$, the homoleptic phosphinoamide complex $[Zr(NPhPPh_2)_4]$ (**1**) is formed (Scheme 3). Similarly, $TiCl_4$ reacts with two equivalents of $LiN(PPh_2)_2$ to give the bisamido complex $[TiCl_2\{N(PPh_2)_2\}_2]$ (**2**) (Scheme 4). The related sulfonamido complexes of zirconium and titanium, $[Zr(NBu^tSPh)_4]$ and $[TiCl_2(NBu^tSPh)_2]$, are also known [31].

Several transition metal [32,33] and lanthanide complexes [34] with phosphinoamido ligands are known; the anionic ligand can be terminal, chelating or bridging.

At room temperature, two signals are observed in the ^{31}P-NMR spectrum of **1** (24.7, s and −5.4 ppm, br, in THF), which are shifted to high field by about 4–34 ppm relative to the phosphinoamine $Ph_2PN(H)Ph$ (28.6 ppm) [26]. At lower temperature, the signal at −5.4 ppm sharpens and the ratio of the two signals changes from ca. 1:1 at 253 K to ca. 1:3 at 223 K. Apparently, at 253 K two of the four phosphino groups in **1** exhibit η^1 coordination in solution (Scheme 3).

Accordingly, similar chemical shifts are observed for the phosphinoamine $[Ph_2PN(H)PPh_2$, 46 ppm (in THF)] [27] and the Ti complex **2** (47 ppm, s). At room temperature, two sets of signals are observed in the ^{31}P-NMR spectrum: a major signal (90%) at 47.0 ppm, corresponding to the tetrahedral symmetric complex, and a minor set (10%) consisting of two small doublets at 5.0 and −10.0 ppm and corresponding to a C_2-symmetric octahedral configuration or to a complex of higher symmetry. The 2D heterocosy spectrum shows that the two doublets are correlated with each other and indicates that, of the many complexes that conceivably be obtained, only one isomer was formed (other possible structures, such as a combination of tridentate and a monodentate ligands, would give rise to additional correlated sets of signals). At 223 K the intensity of the signal at 47.0 ppm decreases, and the intensity of the two doublets increases. Furthermore, small additional signals are observed, presumably due to the formation of other mono-chelated and unsymmetrical complexes. This process is fully reversible on warming the sample to room temperature.

The possible octahedral complexes (I–IV) that can be obtained with these systems are denoted in Scheme 5. As can be seen, compounds I, III and IV are expected to exhibit the same type of signals as described above (two correlated doublets). For complex II, each phosphorus atom is different, and an additional pair of two correlating doublets would be expected. Hence, compound II was not obtained.



Scheme 5.

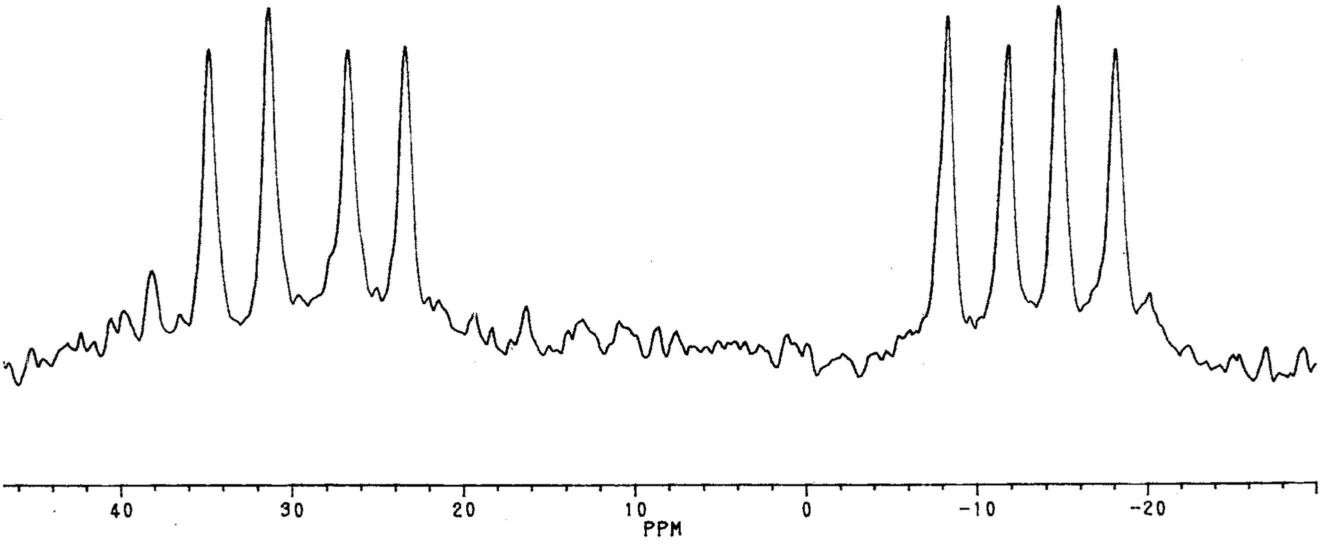


Fig. 1. $^{31}P\{^{1}H\}$-NMR spectrum of complex **2** with MAO at room temperature.

Since the octahedral complex is obtained by a dynamic process, it seems reasonable to expect that both isomers (III and IV) will be obtained as a mixture that would give rise to two different sets of two doublets in the ^{31}P-NMR spectrum. To rule out the formation of complexes III and IV and to support the exclusive formation of the *cis*-octahedral complex with C_2 symmetry, we treated complex **2** with MAO at room temperature and monitored the changes in the ^{31}P-NMR signals. The reaction of MAO with any of the compounds in Scheme 5 will lead to the formation of the corresponding cationic methyl complexes (Scheme 2). With III and IV, a set of two doublets should be obtained for each compound, since two of the four phosphorus atoms are magnetically equivalent. For complex I, with a C_2 symmetry, the phosphorus atoms are inequivalent, and two sets of two doublets are expected. As can be seen in Fig. 1, the ^{31}P-NMR spectrum of complex **2** with MAO exhibits, as expected, four doublets ($^{2}J_{PP} = 278$ Hz), supporting the exclusive formation of the C_2-symmetric *cis*-octahedral complex. Interestingly, in the presence of MAO at room temperature, isomer I is the major isomer present in solution (minor amounts of the tetrahedral complex are also observed), due to the donation of the phosphorus lone pair of electrons to the cationic metal center.

2.2. Molecular structure of **1**

Colorless single crystals of **1** were obtained at room temperature from diethyl ether. The compound crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit (vide infra). There is one disordered Et_2O molecule in the unit cell (O at 1/2 1 1/2). The four $NPhPPh_2$ ligands exhibit η^2 coordination (Fig. 2). The ZrN_4P_4 fragment is highly symmetrical and almost of D_2 symmetry. Hence, the complex is chiral, and both enantiomers cocrystallize in the asymmetric unit. The mirror image of molecule 2 differs from molecule 1 only in the orientation of the phenyl groups. Similar structural features have been observed in homoleptic lanthanide phosphinoamides [34].

Homoleptic eight-coordinate complexes of Group 4 metals with four anionic chelating ligands are known with six-, five-, four- and three-membered metallacycles

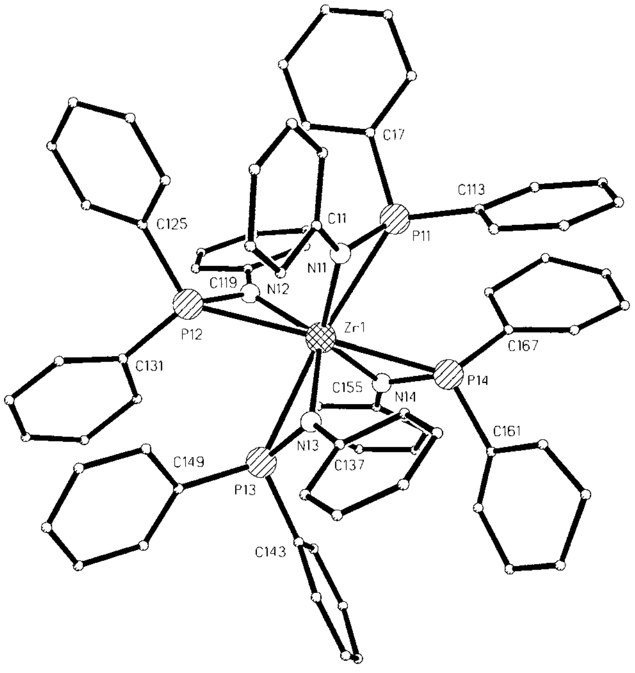


Fig. 2. Molecular structure of **1**. One of the two enantiomers in the asymmetric unit is shown. Hydrogen atoms are omitted for clarity.

(e.g. three-membered rings: pyrazolato complexes of Ti [35], sulfenamido complex of Zr [31], hydroxylamido complex of Ti [36] and Zr [36]). To date, no homoleptic zirconium phosphinoamide complexes were known.

In 1960, Orgel suggested that in eight-coordinate complexes of formula MA_4B_4 the two different donor atoms A and B should occupy the two non-equivalent positions in a dodecahedron [37]. Thus, in complexes with d^0 metal ions, the better π donor should occupy the B coordination sites in a dodecahedron [38]. The coordination polyhedron for an eight-coordinate transition metal complex can be determined by calculating the angle of intersection between the planes of the two interpenetrating BAAB trapezoids of an assumed dodecahedron. This angle is then compared with that of an idealized dodecahedron (90°) and of an idealized square antiprism (74.4°) [39]. For **1**, this angle is 86.4 (for molecule 1) and 86.2° (for molecule 2), and this indicates a distorted dodecahedral coordination environment (max. deviation of N, P from mean planes of trapezoids: 0.24–0.36 Å). The bidentate phosphinoamido ligands span the m edges of the distorted dodecahedron to give the *mmmm* [37b] stereoisomer. This appears to be the preferred stereoisomer in complexes with four bidentate ligands having a small bite angle [40].

The ZrN_4 fragment has a distorted tetrahedral geometry [N–Zr–N range from 97.2(2) to 102.4(2)° and from 131.7(2) to 132.0(2)°], and the ZrP_4 fragment a twisted rectangular arrangement [P–Zr–P range from 75.77(5) to 108.39(5)° and 162.99(5) to 163.88(6)°]. The sum of angles at the nitrogen atoms (C–N–P ca. 130°, C–N–Zr ca. 140°, P–N–Zr ca. 90°, sum: ca. 360°) indicates trigonal-planar coordination. Thus, the phosphinoamide ligand can be regarded as a 4 (N) + 2 (P) electron donor. As in related anionic phosphinoamido complexes of lanthanides, the four NP groups can be described as two N_2P_2 planes, which both form parallelogramms and are staggered with respect to each other. Complex **1** exhibits comparable structural parameters to the zirconium sulfenamido complex $[Zr(NBu^tSPh)_4]$, which also possesses D_2 symmetry and can be regarded as a distorted dodecahedron in which the ZrN_4 tetrahedron is considerably flattened [Zr–N: 2.125(4)–2.147(4), Zr–S: 2.774(2)–2.814(4) Å, N–Zr–N: 95.4(2)–104.7(2), 131.3(2)–132.0(2), S–Zr–S: 79.4(1), 80.8(1), 101.2(1), 102.3(1), 165.3(1) and 165.8(1), Zr–N–S: 92.5(2)–94.2(2), Zr–S–N: 49.1(1)–50.0(1), N–Zr–S: 36.7(1)–37.5(1)°] [31]. Different structural parameters are observed for $[Zr(ONMe_2)_4]$ [36]. The molecule has C_2 symmetry, and the ZrO_4N_4 polyhedron can be described as two interpenetrating strongly distorted MX_4 tetrahedra (O–Zr–O 90.5–131.5, N–Zr–N 90.7–127.8°). Here, the Zr–O(1) bond length is smaller than Zr–O(2) by ca. 0.05 Å, and Zr–N(1) is larger than Zr–N(2) by ca. 1 Å [36].

The Zr–N bond lengths of the Zr–N–P three-membered rings in **1** differ by ca. 0.02 Å [mean Zr–N 2.177(5) Å, range 2.168(5)–2.189(5) Å], and the Zr–P bond lengths by ca. 0.05 Å [mean Zr–P 2.741(2) Å, range 2.711(2)–2.763(2) Å] (Table 1). The Zr–N and the Zr–P distances are longer than those observed for homoleptic amido complexes (e.g. $Zr–N_{terminal}$ in $[Zr(NMe_2)_4]$: 2.050(5)–2.104(5) Å, Zr–N in $[Zr\{NH(2,6\text{-}Pr^i_2C_6H_3)\}_4]$: 2.027(7)–2.057(7) Å) [41] and zirconocene phosphine complexes (e.g. Zr–P in $[Cp_2Zr(PMe_3)_2]$: 2.650(2), 2.638(2) Å; in $[Cp_2Zr(C_2H_4)(PMe_3)]$: 2.693(2) Å) [42].

The structural data of the $NPhPPH_2$ ligands [P–N 1.638(7)–1.682(6) Å] are only slightly different from those of the free ligand $Ph_2PN(H)Ph$ [P–N 1.696(3) Å] [34].

2.3. Catalytic polymerization studies

The polymerization of propylene was carried out with precursors **1** and **2**, which were activated by MAO in toluene. To this mixture propylene was added under a pressure that maintained it at all times as liquid propylene. After a measured time interval, the reaction was quenched by the addition of HCl–MeOH. Subsequently, the polymer was washed with water and acetone, followed by multiple extractions with hot heptane before drying the polymer under vacuum. In all cases, no low-molecular-weight atactic polypropylene was observed.

Table 2 shows the propylene polymerization results obtained with the catalytic systems **1**/MAO and **2**/MAO. The activity of the titanium complex **2** was found to be much higher than that of the corresponding zirconium complex **1** under the same experimental conditions (entries 2 and 6). The polymerization reactions were carried out in liquid propylene (highest monomer concentration) to avoid, as much as possible, the epimerization of the last-inserted unit, as found for other octahedral complexes (Scheme 1), and to allow rational design of an elastomeric polymer. The formation of an elastomeric polypropylene (no atactic high-molecular-weight polymer was observed; vide infra) is consistent with the proposed equilibrium between a *cis*-octahedral and a tetrahedral active cationic catalyst, as presented in Scheme 2.

The polymer microstructures of the elastomeric polypropylene products were characterized by standard ^{13}C-NMR analytical methods and measured at 135°C in 1,2,4-trichlorobenzene [43]. Fig. 3 shows the ^{13}C-NMR spectrum of the elastomeric polymer obtained under the conditions of entry 6 (Table 2). In the methyl region it exhibits a high-intensity signal (35%) corresponding to the *mmmm* pentad, and this rules out the possibility that high-molecular-weight atactic polypropylene was obtained. (All the extracted and

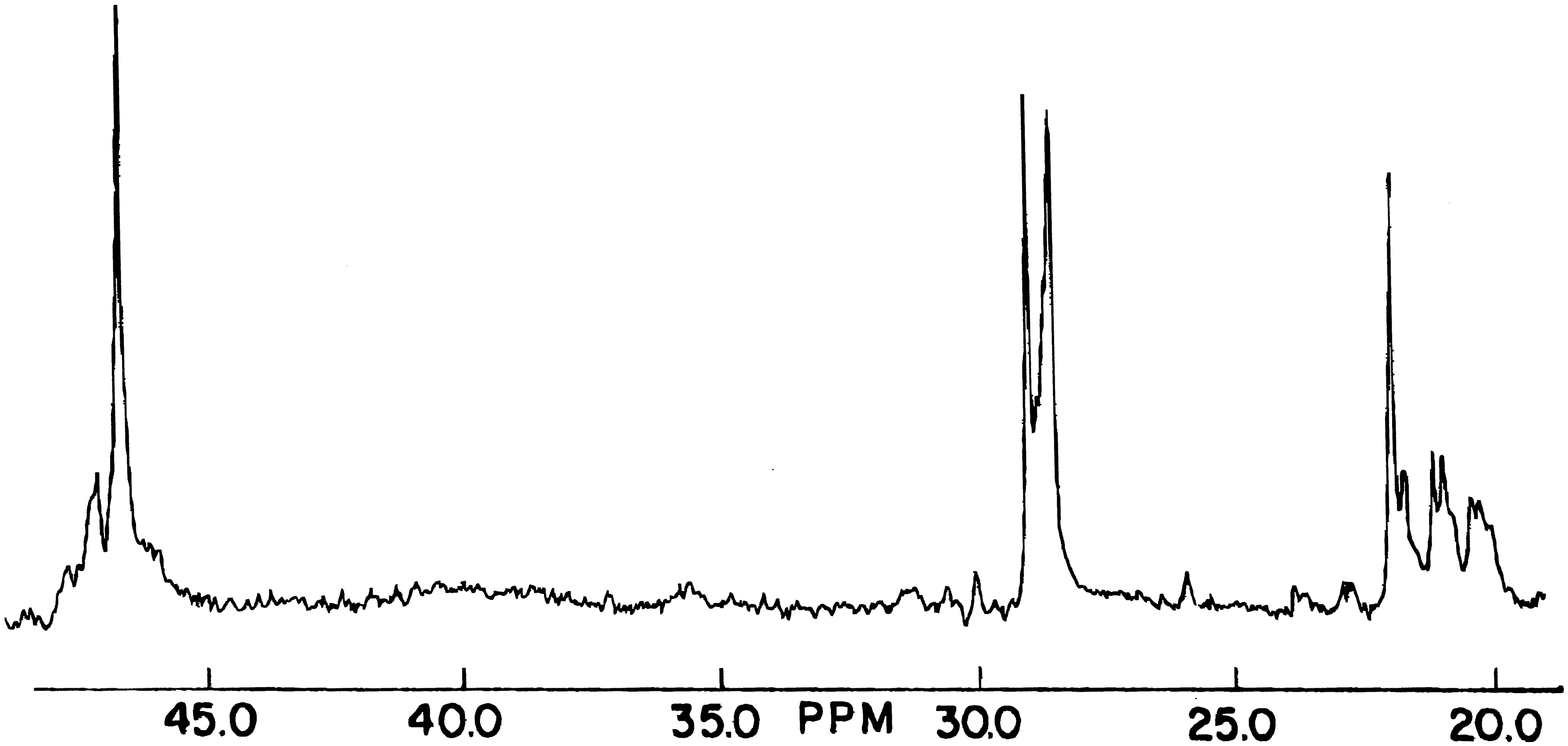


Fig. 3. $^{13}C\{^{1}H\}$-NMR spectrum of the elastomeric polypropylene at 135°C in 1,2,4-trichlorobenzene.

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

Molecule 1			
Zr(1)–N(13)	2.168(5)	Zr(1)–N(14)	2.175(5)
Zr(1)–N(11)	2.173(5)	Zr(1)–N(12)	2.181(5)
Zr(1)–P(14)	2.729(2)	Zr(1)–P(13)	2.733(2)
Zr(1)–P(12)	2.744(2)	Zr(1)–P(11)	2.762(2)
P(11)–N(11)	1.680(5)	P(12)–N(12)	1.670(5)
P(13)–N(13)	1.666(5)	P(14)–N(14)	1.646(6)
N(13)–Zr(1)–N(14)	101.6(2)	N(13)–Zr(1)–N(11)	97.2(2)
N(14)–Zr(1)–N(11)	132.0(2)	N(13)–Zr(1)–N(12)	131.7(2)
N(14)–Zr(1)–N(12)	97.3(2)	N(11)–Zr(1)–N(12)	102.4(2)
P(14)–Zr(1)–P(13)	100.93(6)	P(14)–Zr(1)–P(12)	163.88(6)
P(13)–Zr(1)–P(12)	79.50(5)	P(14)–Zr(1)–P(11)	75.77(5)
P(13)–Zr(1)–P(11)	162.99(5)	P(12)–Zr(1)–P(11)	108.39(5)
N(13)–Zr(1)–P(14)	90.8(2)	N(14)–Zr(1)–P(14)	37.1(2)
N(11)–Zr(1)–P(14)	99.6(2)	N(12)–Zr(1)–P(14)	128.0(2)
N(13)–Zr(1)–P(13)	37.6(1)	N(14)–Zr(1)–P(13)	88.1(1)
N(11)–Zr(1)–P(13)	129.6(1)	N(12)–Zr(1)–P(13)	100.1(2)
N(13)–Zr(1)–P(12)	98.7(1)	N(14)–Zr(1)–P(12)	127.4(2)
N(11)–Zr(1)–P(12)	92.2(2)	N(12)–Zr(1)–P(12)	37.5(1)
N(13)–Zr(1)–P(11)	125.4(1)	N(14)–Zr(1)–P(11)	98.1(2)
N(11)–Zr(1)–P(11)	37.5(1)	N(12)–Zr(1)–P(11)	94.8(2)
N(11)–P(11)–Zr(1)	51.9(2)	N(12)–P(12)–Zr(1)	52.6(2)
N(13)–P(13)–Zr(1)	52.5(2)	N(14)–P(14)–Zr(1)	52.9(2)
Molecule 2			
Zr(2)–N(23)	2.172(5)	Zr(2)–N(22)	2.176(5)
Zr(2)–N(24)	2.179(5)	Zr(2)–N(21)	2.189(5)
Zr(2)–P(21)	2.711(2)	Zr(2)–P(22)	2.739(2)
Zr(2)–P(23)	2.750(2)	Zr(2)–P(24)	2.763(2)
P(21)–N(21)	1.648(5)	P(22)–N(22)	1.672(5)
P(23)–N(23)	1.680(5)	P(24)–N(24)	1.678(5)
N(23)–Zr(2)–N(22)	131.3(2)	N(23)–Zr(2)–N(24)	104.7(2)
N(22)–Zr(2)–N(24)	97.2(2)	N(23)–Zr(2)–N(21)	95.4(2)
N(22)–Zr(2)–N(21)	101.4(2)	N(24)–Zr(2)–N(21)	131.9(2)
P(22)–Zr(2)–P(23)	77.41(5)	P(21)–Zr(2)–P(24)	78.71(5)
P(22)–Zr(2)–P(24)	160.97(6)	P(23)–Zr(2)–P(24)	108.30(5)
N(23)–Zr(2)–P(21)	129.9(1)	N(22)–Zr(2)–P(21)	85.4(1)
N(24)–Zr(2)–P(21)	101.9(1)	N(21)–Zr(2)–P(21)	37.4(1)
N(23)–Zr(2)–P(22)	96.8(1)	N(22)–Zr(2)–P(22)	37.6(1)
N(24)–Zr(2)–P(22)	126.6(1)	N(21)–Zr(2)–P(22)	92.7(1)
N(23)–Zr(2)–P(23)	37.6(1)	N(22)–Zr(2)–P(23)	100.5(1)
N(24)–Zr(2)–P(23)	90.9(1)	N(21)–Zr(2)–P(23)	127.8(1)
N(22)–Zr(2)–P(24)	123.9(1)	N(23)–Zr(2)–P(24)	98.2(1)
N(24)–Zr(2)–P(24)	37.4(1)	N(21)–Zr(2)–P(24)	97.4(1)
P(21)–Zr(2)–P(22)	100.25(5)	P(21)–Zr(2)–P(23)	165.22(6)
N(21)–P(21)–Zr(2)	53.8(2)	N(22)–P(22)–Zr(2)	52.6(2)
N(23)–P(23)–Zr(2)	52.2(2)	N(24)–P(24)–Zr(2)	52.1(2)
Both molecules			
P–C	1.807(9)–1.854(6)	N–C	1.406(7)–1.447(8)
N–P–C	108.7(5)–115.4(4)	C–P–C	102.4(3)–105.5(3)
C–P–Zr	125.4(2)–132.2(2)	C–N–P	128.7(4)–131.8(4)
C–N–Zr	138.4(4)–141.0(4)	P–N–Zr	88.7(2)–90.7(2)

washed polymers obtained as shown in Table 2 show similar behaviour, with intense *mmmm* pentad signals in the ^{13}C-NMR spectrum) [44]. Thus, the ^{13}C-NMR spectrum indicates polymer molecules with a combination of atactic and isotactic blocks and a large domain of isotactic pentads, as expected for elastomeric polymers [24,25,45]. In the ^{1}H-NMR spectrum, no vinylidene or vinyl chain end groups were detected, suggesting an aluminum chain transfer mechanism as the major termination step. Note that in Fig. 3, additional signals appear in the methyl region, indicating an apparently low resolution spectrum. A simple comparison with other signals in the spectrum (25 and 48 ppm) shows that this broadness is the result of different environments of the methyl protons besides the ten expected isotactic-atactic signals (vide infra).

Interestingly, the activation of complex **1** by MAO implies that two of the amido groups are exchanged for methyl groups, followed by the removal of a methyl group to give the corresponding cationic complex. We have recently shown that in the reaction of simple tetrahedral homoleptic tetraamido Group 4 complexes with methylalumoxane (MAO), two of the four amido groups are replaced by methyl ligands, with the subsequent formation of the active cationic catalysts for the rapid polymerization of ethylene and the atactic polymerization of propylene [7,9].

Comparison of the relationships between activity, co-catalyst concentrations and temperature shows that in contrast to the octahedral benzamidinate complexes, the catalytic activity increases with increasing MAO:catalyst ratio and temperature. This behaviour is believed to be a result of the low coordinative unsaturation and increased electrophilicity of the metal center, on increasing the MAO concentration, which favours the coordination of the incoming monomer to the active 'cationic' complex. Increasing the temperature results in a faster process, and this suggests that the cationic complexes are highly stable [6].

For both catalyst systems, the molecular weights of the elastomeric polymers are similar with narrow polydispersities. This result supports a polymerization mechanism in which a single-site catalyst is responsible for the formation of the elastomeric polypropylenes.

The results presented here show that octahedral 'cationic' complexes with C_2 symmetry can induce the formation of isotactic polypropylene, whereas tetrahedral complexes of C_{2v} symmetry lead to atactic polypropylene. The rapid and dynamic interconversion of these two structures leads to elastomeric polymers. The homo-copolymer (isotactic-atactic block copolymer) can be easily tailored by changing the donor strength of the dynamic pendant atoms, allowing the formation of either short or large isotactic blocks between the atactic blocks. This type of polymer has been obtained with non-bridged metallocene complexes in which the rotational frequency of the substituted cyclopentadienyl ligands allows an exchange between C_2

Table 2
Activity data for the polymerization of propylene promoted by complexes **1** and **2** activated by MAO in liquid propylene

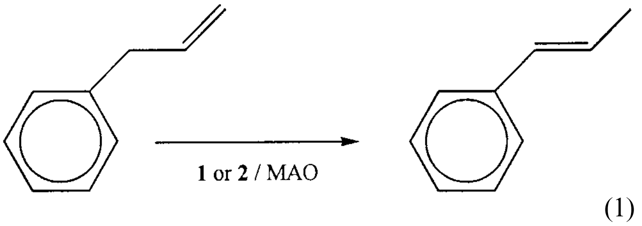
Entry	Catalyst	Temperature (°)	Ratio MAO:complex	Activity g polymer/mol h	M_w	M_n	M_w/M_n
1	2	0	500	890			
2	2	25	500	1570	145620	88240	1.65
3	2	0	1000	1450			
4	2	25	1000	4190	163840	104470	1.57
5	2	60	1000	4750			
6	1	25	500	80	115390	48010	2.40

and C_{2v} symmetries [24,25] and recently with dual-side bridged metallocene complexes [45].

To corroborate that the epimerization mechanism is responsible for the formation of elastomeric polypropylene, we treated 1-octene with complex **1** activated by MAO. Since the olefin is expected to polymerize much slower than propylene, the epimerization mechanism, if applicable, should induce the isomerization of α-olefins to the corresponding internal olefins. A β-hydrogen elimination is expected to occur either from the methyl group at the β-position in the intermediate complex B (Scheme 6, R = H, without causing any change in the alkene), or from the β-position at the alkyl chain, inducing the isomerization of the double bond.

The isomerization of 1-octene promoted by complex **1** and MAO resulted in the quantitative formation of *trans*-2-octene. The isomerization of 1-octene with complex **2** leads to the formation of *trans*-2-octene (95%) and small amounts (~5%) of *cis*-2-octene, (*E*)-3-octene, (*E*)-4-octene and a myriad of saturated and unsaturated dimers, trimers and tetramers (the latter observed by GC-MS). The treatment of *trans*-2-octene with **2**/MAO resulted in slow isomerization to *cis*-2-octene (up to 5% conversion after 16 h at 80°C), with traces of the oligomeric compounds, indicating that the process is fully in equilibrium.

The reactions of allylbenzene with catalysts **1** or **2** activated by MAO, induces selectively the formation of *trans*-methylstyrene (Eq. (1)). For complex **1** the reaction is extremely fast, producing 100% conversion at room temperature in 15 min, whereas for complex **2**, 77% yield was obtained after 16 h at 80°C [46].



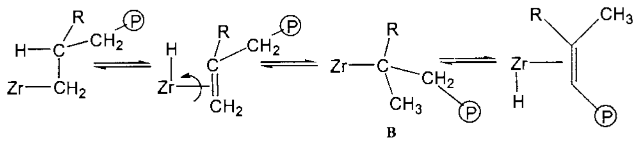
(1)

These isomerization results indicate that during polymerization the metal center is also able to migrate through the growing polymer chain, inducing branching and additional environments for the methyl ligands, as shown in Scheme 6 [47].

Thus, simple tetrahedral complexes with ancillary ligands incorporating donating groups (with a lone pair of electrons able to coordinate to the metal center) allows the rational design of selective elastomeric polypropylenes.

3. Experimental

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture. Argon, propylene and nitrogen gases were purified by passage through a MnO oxygen-removal column and a Davison 4Å molecular sieve column. Ether solvents (THF-d_8) were distilled under argon from sodium benzophenone ketyl. Hydrocarbon solvents (toluene-d_8, benzene-d_6) were distilled under nitrogen from Na/K alloy. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable bulbs or freshly distilled prior to use. For **1**, the NMR spectra were recorded with an AVANCE DRX 400 spectrometer (Bruker), for **2** on a Bruker AM 200 and a Bruker AM 400 spectrometer. ^{1}H-NMR: internal standard solvent, external standard TMS; ^{13}C-NMR: external standard TMS, internal standard solvent; ^{31}P-NMR: external standard 85% H_3PO_4. The IR spectrum of **1** was recorded on a FTIR spectrometer Perkin–Elmer System 2000 in the range 350–4000 cm^{-1}. GC-MS experiments were conducted in a GCMS (Finnigan Magnum) spectrometer. The melting points were determined in sealed capillaries under argon and are uncorrected. Molecular weights were measured with a Waters GPCV 150 plus instrument



For 1-octene: R=H ; Ⓟ = $(CH_2)_4CH_3$

Scheme 6. Plausible isomerization pathway for 1-octene in the presence of complex **1**.

calibrated against polystyrene. $LiNPhPPh_2$ [28] and $[Li(THF)N(PPh_2)_2]_2$ [29] were prepared according to the literature procedure. $TiCl_4$, $ZrCl_4$, $HN(SiMe_3)_2$, *n*-BuLi (solution in hexane) (all Aldrich), Ph_2PCl (Strem) are commercially available. α-Olefins (1-octene, 2-octene, allylbenzene) were dried and stored over activated molecular sieves (4Å), degassed, and freshly vacuum-distilled.

3.1. *$[Zr(NPhPPh_2)_4]$* (**1**)

A solution of 4.27 g (10.0 mmol) $LiNPhPPh_2$ in 50 ml diethyl ether was added dropwise to a stirred suspension of 0.58 g (2.5 mmol) $ZrCl_4$ in 100 ml diethyl ether at −78°C. The solution was stirred overnight at room temperature (r.t.). Then LiCl was filtered off and the solvent partially removed in vacuo until ca. 40 ml of the solution remained. Colourless crystals of **1** were obtained at −30°C. Yield 65%. M.p. 180–182°C. $C_{72}H_{60}N_4P_4Zr$ (1196.34); Calc.: C, 72.31; H, 5.02; N, 4.67; P, 10.38; Found: C, 72.13; H, 5.07; N, 4.58; P, 10.51%. ^{1}H-NMR (C_6D_6): δ 6.69–7.74 (m, Ph). ^{31}P-NMR (THF, 283 K): δ 24.2 (s), −5.4 (s).

3.2. *$[TiCl_2\{N(PPh_2)_2\}]$* (**2**)

To a stirred solution of $[Li(THF)N(PPh_2)_2]_2$ (2.0 g, 2.16 mmol) in 50 ml THF, was added $TiCl_4$ (0.24 ml, 2.16 mmol) dropwise at r.t. The reaction mixture was stirred overnight, the solvent removed in vacuum and the residue was extracted with 30 ml of toluene. Hexane was added to the filtrate to precipitate a brown solid, which was recrystallized from dichloromethane at −78°C. Yield 35%. M.p. 120°C (dec.). $C_{48}H_{40}Cl_2N_2P_4Ti$ (887.5); Calc.: C, 64.96; H, 4.54; N, 3.16; Found: C, 64.03; H, 4.86; N, 3.01. ^{1}H-NMR (THF-d_8): δ 7.0–8.2 (m, Ph). ^{31}P-NMR (THF): δ 47.0 (s).

3.3. *Polymerization experiments*

These experiments were conducted in a 100 ml flamed round-bottom reaction flask attached to a high-vacuum line. In a typical experiment 4.0 mg of the catalyst **1** and 205 mg of MAO (Zr:Al = 1:400) were charged in the flask containing a magnetic stir bar. The reaction vessel was connected to a high-vacuum line, pumped down and back-filled three times with argon. Then the flask was re-evacuated, 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) the polymerization was quenched by releasing the excess pressure of propylene and immediately injecting a methanol–HCl mixture. The polymeric product was collected by filtration, washed with hexane and acetone and dried under vacuum for several hours.

3.4. *Isomerization experiments*

In a typical procedure, an olefin (0.1 ml) was vacuum transferred into a J-Young NMR tube containing 10 mg of catalyst and MAO (MAO:catalyst = 400) in 0.6 ml of toluene-d_8. The sealed tube was then heated in an oil bath at 80°C. The organic products were vacuum transferred (10^{-6} mmHg) to another J-Young NMR tube and sealed, and both residue and volatiles were characterized by ^{1}H- and ^{13}C-NMR spectroscopy, GC-MS and comparison with known compounds [46].

3.5. *Crystallographic studies*

Data of **1** (Mo–K_α, $\lambda = 0.71073$ Å) were collected with 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 [48]) and subsequent difference Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL PLUS [48]). Restrictions for **1**: C, N, P, and Zr atoms anisotropic, H atoms located and refined isotropically. Absorption correction with SADABS.

Crystal data for **1**·1/4Et_2O: $C_{72}H_{60}N_4P_4Zr \cdot 1/4Et_2O$, $M = 1214.87$, colourless crystals, triclinic, space group $P\bar{1}$ (no. 2), $T = 213(2)$ K, $a = 12.834(1)$, $b = 21.874(1)$, $c = 23.975(1)$ Å, $\alpha = 86.81(1)$, $\beta = 77.53(1)$, $\gamma = 81.86(1)°$, $V = 6503.0(2)$ Å^3, $Z = 4$, $D_{calc} = 1.241$ Mg m^{-3}, $F(000) = 2522$, μ(Mo–K_α) = 0.312 mm^{-1}, 40265 reflections collected with $0.87 < \theta < 27.24°$; of these, 24841 were independent; 1502 parameters, refinements converge to $R_1 = 0.0714$, $wR_2 = 0.2108$ (for reflections with $I > 2\sigma(I)$), $R_1 = 0.1325$, $wR_2 = 0.2613$. Even though the outer shape and size of the crystals appeared in good order, the data set obtained was of rather low quality [$R_{int} = 0.0458$]. Recrystallization and several attempts to remeasure different crystals did not result in a better data set.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (**1**: CCDC no. 145086). 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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