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PPh-bridged metallocene complexes of the type $(C_{13}H_8{-}PPh{-}C_{13}H_8)MCl_2$ (M = Zr, Hf)

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Abstract

The synthesis and NMR spectroscopic characterization of new *ansa*-metallocene dichloride complexes of the type $(C_{13}H_8{-}PPh{-}C_{13}H_8)MCl_2$ (M = Zr (**5**), Hf (**6**)) is reported The complexes can be activated with methylaluminoxane (MAO), and are then able to polymerize ethylene. In contrast to CR_2 and SiR_2 bridged derivatives, the PPh bridge increases the electron density of the system which leads to a drastic decrease in polymerization activities. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: *ansa*-Metallocene complexes; PPh-bridge; Zirconium; Hafnium; Catalysis; Olefin polymerization

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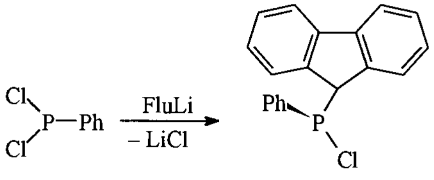
1. Introduction

ansa-Metallocene complexes possess a remarkable potential as catalysts for olefin polymerization [1–3]. The structure of the bridge greatly impacts the polymerization behavior of these catalysts. The substitution of a methylene bridge by a silylene group, for example, leads to higher activities for ethylene polymerization without lowering the molecular weight or the crystallinity of the polymers [1–4]. Bridging groups containing silicon, germanium and tin reduce the syndiotacticity of the polypropylenes they generate [5]. Until now, only cyclopentadienyl derivatives of –PR–bridged metallocene complexes have been synthesized [6,7]. The polymerization behavior of these complexes was studied in none of the previous investigations. The electron donating capability of the –PR– moiety should impact the polymerization activity of the corresponding *ansa*-metallocene complexes. If the insertion of the olefin into the Zr–C bond is the rate determining step, then the higher electron density at the metal should cause a stronger carbon–metal bond with the effect of a decrease in activity.

2. Results and discussion

2.1. Synthesis of the ligand precursors

The reaction of phenyl dichlorophosphine with one equivalent of fluorenyllithium leads to fluorenyl phenyl chloro phosphine (**1**), a good starting compound for the synthesis of a mixed substituted phosphine.



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Compound **1** reacts quantitatively with indenyllithium to form fluorenyl indenyl phenyl phosphine (**2**) as a mixture of isomers:

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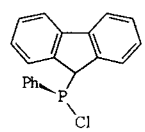
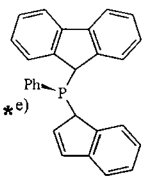
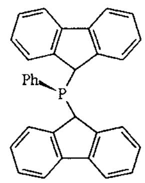
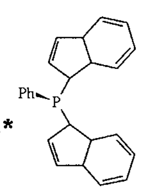
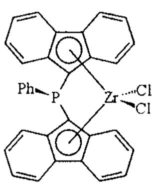
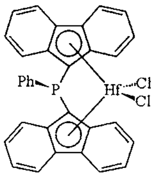
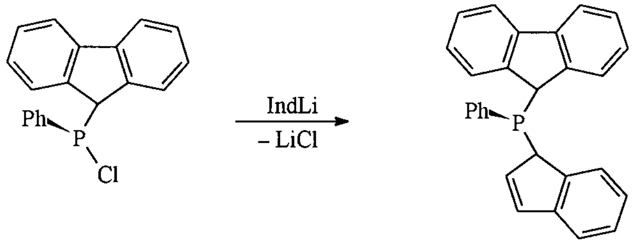
Table 1
NMR data of **1**–**6** (250.13 MHz (^{1}H), 69.2 MHz (^{13}C))

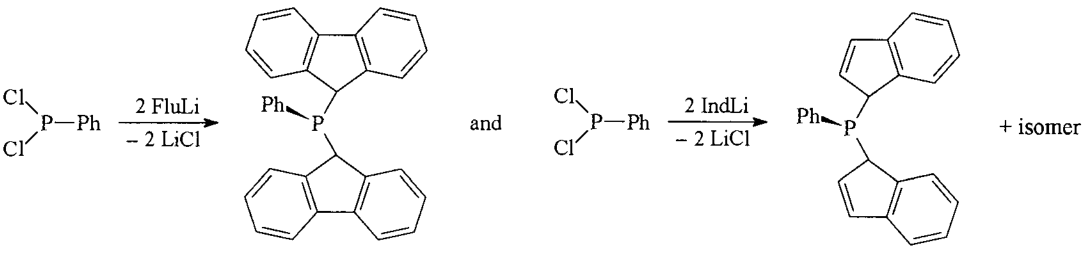
	^{1}H-NMR[a]	^{13}C-NMR[a]	^{31}P-NMR[a]
1 	7.74-7.60 (3H)[c], 7.40-7.15 (9H), 7.03 (m, 1H), 4.78 (d, $^2J(^1H,^{31}P)$ 22.9 Hz, 1H)	n.d.[b]	91.6
2/2*[e] 	7.78-7.73 (2H)[c], 7.58-7.53 (5H)[c], 7.35-7.08 (14H)[c], 7.05-6.97 (6H)[c], 6.82-6.80 (m, 1H), 6.72-6.65 (m, 2H), 6.64-6.57 (m, 2H), 6.47-6.42 (m, 1H), 6.38-6.33 (m, 1H), 5.03 (d, $^2J(^{31}P,^1H)$ 3.8 Hz, 2H, **CH**$_{flu}$), 4.67 (s, 1H, **CH**$_{ind}$), 2.72 (m, 1H, **CH**$_{ind}$), 2.67 (m, 1H, **CH**$_{ind}$)	[d] 47.4 (d, $^1J(^{31}P,^{13}C)$ 22.0 Hz, CH$_{ind}$), 45.2 (d, $^1J(^{31}P,^{13}C)$ 29.2 Hz, CH$_{flu}$), 44.5 (d, $^2J(^{31}P,^{13}C)$ 7.6 Hz, CH$_{ind}$)	-7.7
3 	7.90-7.87 (2H)[c], 7.73-7.67 (4H)[c], 7.37-7.23 (8H)[c], 7.20-7.06 (3H)[c], 6.83 (t, $^3J(^1H,^1H)$ 7.1 Hz, 2H), 6.70 (t, $^3J(^1H,^1H)$ 7.2 Hz, 2H), 5.18 (s, 1H, **CH**), 5.17 (s, 1H, **CH**)	143.6, 141.4 (C$_q$)[f], 134.2, 133.8, 129.3, 127.0, 126.7, 126.6, 126.5, 125.3, 125.2, 125.1, 125.1, 120.2, 120.1, 45.5, 45.1 (CH)	9.7
4/4* 	7.65-7.46 (4H)[c], 7.39-7.33 (4H)[c], 7.22-7.17 (5H)[c], 6.35-6.32 (2H)[c], 3.47-3.45 (4H)[c]	145.9, 144.2, 144.1 (C$_q$), 141.7, 141.6 (CH), 140.0, 139.8 (C$_q$), 134.2, 133.9, 129.1, 128.6, 128.4, 126.2, 125.0, 124.9, 123.6, 121.4, 121.3 (CH), 39.9, 39.8 (CH$_2$)	-39.7
5 	8.18-8.12 (2H)[c], 8.06-8.03 (2H)[c], 7.85-7.82 (4H)[c], 7.60-7.57 (2H)[c], 7.38-7.08 (9H)[c], 6.87-6.81 (2H)[c]	134.2, 133.8 (CH), 133.1, 133.0, 131.7, 131.1 (C$_q$), 130.8, 130.5 (CH), 129.3, 129.1 (C$_q$), 129.1, 129.0, 129.0 (CH), 127.8 (C$_q$), 127.3, 127.3, 127.0, 126.8, 126.6, 126.5, 126.2, 126.1 (CH), 126.0 (C$_q$), 125.1, 124.8, 124.3, 120.3, 120.1 (CH)	-42.3
6 	8.18-8.12 (2H)[c], 8.06-7.88 (4H)[c], 7.85-7.82 (m, 4H), 7.60-7.47 (2H)[c], 7.40-7.14 (7H)[c], 6.85-6.79 (2H)[c]	134.2, 133.8 (CH), 133.1, 133.0, 131.7, 131.1 (C$_q$), 130.8, 130.5 (CH), 129.3, 129.1 (C$_q$), 129.1, 129.0, 129.0 (CH), 127.8 (C$_q$), 127.3, 127.3, 127.0, 126.8, 126.6, 126.5, 126.2, 126.1 (CH), 126.0 (C$_q$), 125.1, 124.8, 124.3, 120.3, 120.1 (CH)	-43.3

[a] In $CDCl_3$ (saturated solution) at 25°C.
[b] n.d., not determined.
[c] Indicated as shift region due to signal overlaps.
[d] The signals of the aromatic carbon atoms were not completely resolved.
[e] A complete spectroscopic analysis of isomer mixtures was not performed.
[f] ^{13}C-NMR signals not completely separated due to overlapping.



1 **2/2***

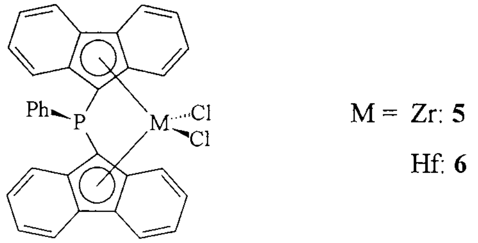
To synthesize symmetrically substituted phosphines, phenyl dichloro phosphine is reacted with two equivalents of fluorenyllithium or indenyllithium to form the corresponding PPh-bridged ligand precursors **3** and **4**.



3 **4/4***

2.2. Synthesis of the metallocene dichloride complexes

The synthesis of the metallocene dichloride complexes is carried out using a standard method. Compound **3** is reacted in diethylether with two equivalents of *n*-butyllithium to form the dianion which is then reacted with zirconium tetrachloride or hafnium tetrachloride to give the metallocene complexes **5** and **6**.



2.3. NMR spectroscopic characterization

The ^{1}H- and ^{13}C-NMR spectra of **5** and **6** are not very meaningful because only aromatic protons and carbon atoms are present. The ^{31}P-NMR signals are characteristic for these compounds and their purity. The ^{31}P-NMR signals of phenyl dichlorophosphine appear at $\delta = 162.1$ ppm. The substitution of one chlorine atom by one fluorenyl ligand (**1**) leads to a high field shift of approximately 70 ppm to $\delta = 91.6$ ppm. Further substitution of chlorine by fluorenyl (**3**) shifts the signal to $\delta = 9.7$ ppm ($\Delta\delta = 82$ ppm). The complexation of the ligand precursor (**5** and **6**) enhances the high field shift of the ^{31}P resonance signal to $\delta = -42.3$ ppm (**5**) or to $\delta = -43.3$ ppm (**6**). The resonance signals of compounds **1**–**6** are listed in Table 1.

2.4. Polymerization of ethylene

Complex **5** was activated with MAO and tested as catalyst for ethylene polymerization. As expected, **5** proved to be less active than the analogous SiR_2 [8] or C_2 bridged [9] bis(fluorenylidene) complexes (Table 2).

3. Experimental

3.1. General procedure

All operations were routinely carried out using Schlenk technique (exclusion of air and moisture). The solvents diethylether, *n*-hexane, *n*-pentane, tetrahydrofuran and toluene were distilled under inert gas (argon) over sodium/potassium alloy. Methylene chloride was dried over calcium hydride. For NMR spectroscopy, deuterated solvents were dried over molecular sieves (300 pm), degassed and stored under inert gas.

Ice (0°C) or dry ice–isopropanol cooling mixtures (-78°C) were used to maintain low temperatures.

Table 2
Ethylene polymerization results for **5**

Activity[a] [g] PE/[mmol] Zr·h ($T_{i,\max}$)[b] (°C)	M_η (g mol^{-1})	α[c] (%)	DSC m.p.[d] (°C) ΔH_m (J g^{-1})
2544 (60.6)	430 000	26	138.08 76.62

[a] [Zr]:[Al] = 1:17 000.

[b] $T_{i,\max}$, maximum inside temperature of the polymerization reactor.

[c] See [10].

[d] The maximum of the melting peak for the second heating run was selected as melting point.

3.2. Chemicals

Fluorene and indene (Fluka) were purified by filtration of their pentane solutions over silica.

Methylaluminoxane (Witco, Bergkamen) was used as a 30 wt.% solution in toluene (average molecular weight 1100 g mol^{-1}; total aluminum content 13.1 wt.% Al with 3.5 wt.% as trimethylaluminum).

All other commercially available chemicals were employed without further purification.

3.3. NMR spectroscopy

The NMR spectrometers Jeol JNM-EX 270 E, Bruker ARX 250 and Bruker DRX 500 were available to record the NMR spectra. The samples were filled under argon and routinely measured in $CDCl_3$ at 25°C. The chemical shifts in ^{1}H-NMR spectra refer to the residual proton signal of the solvent ($\delta = 7.24$ for $CHCl_3$), the shifts in the ^{13}C-NMR spectra to the solvent signal ($\delta = 77.0$ for $CDCl_3$) and in ^{31}P-NMR spectra to the resonance of external aqueous phosphoric acid ($\delta = 0.0$).

3.4. Mass spectroscopy

Routine measurements were performed with a Varian MAT CH7 instrument (direct inlet system, electron impact ionization 70 eV). GC/MS spectra were recorded using a Varian 3700 gas chromatograph in combination with a Varian MAT 312 mass spectrometer.

3.5. Gas chromatography

A Carlo Erba HRGC gas chromatograph with flame ionization detector was used to analyze organic compounds. The gas chromatograph was equipped with a 30 m long J&W fused silica column (DB1, film thickness 0.25 μm). Helium served as carrier gas; the flow through the column was 3.8 ml min^{-1}, split 1:30, septum flushing 1.3 ml min^{-1}. The following temperature program was routinely used: 3 min at 50°C (starting phase), 5 K min^{-1} (heating phase), 15 min at 310°C (plateau phase). The retention time was indicated in seconds.

3.6. Characterization of the polymer samples

3.6.1. Differential scanning calorimetry

A Perkin Elmer DSC-7 calorimeter was available to measure the thermal properties of the polymer samples. Prior to the measurements, the polymer samples were dried in vacuo. To determine the fusion enthalpies, 3–5 mg of the polymer were fused into standard aluminum pans and measured using the following temperature program: first heating phase (20 K min^{-1}) from 50 to 200°C, first cooling phase (-20 K min^{-1}) -50°C, second heating phase (20 K min^{-1}) from 50 to 200°C, second cooling phase (-20 K min^{-1}) -50°C. The temperature was linearly corrected relative to indium (m.p. 156.6°C); the fusion enthalpy of indium ($\Delta H_m =$ 28.45 J g^{-1}) was used for calibration. To determine the crystallinity degree α, the relationship $\alpha = \Delta H_m/\Delta H_m^0$ was used. ΔH_m derives from the data of the second heating course of the DSC. ΔH_m^0 as fusion enthalpy for 100% crystalline polyethylene was assumed to be 290 J g^{-1} [10].

3.6.2. Viscosimetry

The intrinsic viscosity $\bar{M}_\eta$ was determined using an Ubbelohde precision capillary viscometer in *cis*/*trans* decalin at 135 ± 0.1°C. Prior to the measurements, the samples were weighed into sealable small flasks and dissolved in an exactly measured amount of decalin at 140–150°C over a period of 3–4 h. Calibration curves were available for the determination of $\bar{M}_\eta$. Each polymer sample was weighed and measured twice to reduce the error.

3.7. Synthesis of fluorenyl phenyl chloro phosphine (**1**)

At -78°C, 18.8 ml *n*-butyllithium (1.6 M in hexane) were added dropwise to a solution of 5.0 g (30 mmol) fluorene in 100 ml diethylether. The solution was stirred for 6 h at room temperature. The solvent was evaporated and the residue washed twice with 50 ml pentane and then dried under high vacuum. Fluorenyllithium remained as a yellow solid. At -78°C, the solids were added to a solution of 8.07 g (45.0 mmol) phenyl dichloro phosphine and 200 ml pentane. Immediately, a white precipitate was formed. The reaction mixture was stirred overnight at room temperature. For processing and separation of unsubstituted and disubstituted side products, the reaction mixture was filtered over sodium sulfate, the residue washed twice with 20 ml pentane and the product extracted with diethylether. After the solvent was evaporated, the product remained as white powder. Yield: 3.7 g (40%).

3.8. Synthesis of fluorenyl indenyl phenyl phosphine (**2**)

At -78°C, 4.0 ml *n*-butyllithium (1.6 M in hexane) were added dropwise to a solution of 0.75 ml (6.5 mmol) indene in 30 ml diethylether. The mixture was stirred for 6 h at room temperature. At -78°C, 2.0 g (6.5 mmol) fluorenyl phenyl chloro phosphine (**1**) were added to the solution and the reaction mixture was stirred overnight at room temperature. For processing, the reaction mixture was filtered over sodium sulfate, the residue washed twice with 20 ml pentane and the product extracted with toluene. After the evaporation of the solvent the product remained as yellow powder. Yield: 1.25 g (80%).

3.9. Synthesis of the –PPh-bridged ligand precursors **3** and **4**

At – 78°C, 37.6 ml *n*-butyllithium (1.6 M in hexane) were added dropwise to a solution of 10.0 g (60.1 mmol) fluorene or 7.0 ml (60.1 mmol) indene in 100 ml diethylether. The mixture was stirred for 6 h at room temperature. At – 78°C, 5.38 g (30.0 mmol) phenyl dichloro phosphine were added to the solution and the reaction mixture was stirred overnight at room temperature. For processing, the reaction mixture was filtered over sodium sulfate, the residue washed twice with 20 ml pentane, and the product extracted with methylene chloride. After the evaporation of the solvent the product remained as white powder. Yield: 80%.

Bis-(9,9-fluorenyl)-(phenyl) phosphine (**3**): MS: *m*/*e* 438 (M^+).

Bis-(1,1-indenyl)-(phenyl) phosphine and isomer (**4**): MS: *m*/*e* 338 (M^+).

3.10. Synthesis of the phosphinidene bridged metallocene complexes **5** and **6**

The ligand precursor **3** (3 mmol) was dissolved in 40 ml diethylether and stirred with exactly two equivalents *n*-butyllithium (1.6 M in hexane) for at least 8 h at room temperature. Then one equivalent zirconium tetrachloride or hafnium tetrachloride was added and stirred overnight. For processing, the complex solution was filtered over sodium sulfate. Then, the product was extracted with methylene chloride or toluene and the solvent was evaporated in vacuo.

η^5,η^5-(9,9-Bisfluorenylidene)phenylphosphine zirconium dichloride (**5**): purple crystals. MS: *m*/*e* 598 (M^+).

η^5,η^5-(9,9-Bisfluorenylidene)phenylphosphine hafnium dichloride (**6**): orange crystals. MS: *m*/*e* 685 (M^+).

3.11. Polymerization reactions

3.11.1. Activation of the catalyst precursor

The metallocene dichloride complex **5** was weighed under inert gas (10 ± 0.1 mg) and activated with MAO (1 ml MAO (30% in toluene) per mg metallocene dichloride complex). The solution was diluted with toluene to an extent that approximately 0.2–0.5 mg of the metallocene complex was dissolved in 1 ml toluene. From this solution, approximately 1 mg catalyst was used for polymerization. This solution was used within 60 min.

3.11.2. Polymerization of ethylene

Pentane (500 ml), 7 ml MAO (30% in toluene) and the corresponding amount of catalyst solution ([Zr]:[Al] = 1:17000) were added to a 1 l Buchi laboratory autoclave BEP 280. The reactor was thermostated at 60°C and a constant ethylene pressure of 10 bar was applied. The polymerization was terminated after 1 h by releasing the ethylene.

Acknowledgements

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