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Syntheses of polymethylene bridged dinuclear zirconocenes and investigation of their polymerisation activities

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Abstract

The polymethylene bridged dinuclear zirconocenes $[(CH_2)_n\,(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ ($n = 3$ (**10**), 5 (**11**), 7 (**12**), 9 (**13**)) have been synthesised by treating not only the respective disodium salts of the ligands with two equivalents of $(C_9H_7)ZrCl_3$ in THF, but also the distannylated derivatives of the ligands with two equivalents of $(C_9H_7)ZrCl_3$ in toluene. All complexes are characterised by ^{1}H- and ^{13}C-NMR and mass spectrometry and elemental analysis. It turned out that the values of $\Delta\delta = [\delta_d - \delta_p]$, the chemical shift difference between the distal (δ_d) and proximal (δ_p) protons, for the produced dinuclear compounds (0.1 for **10** and **11**, and 0.11 for **12** and **13**) were smaller than the $\Delta\delta$ values of the known polysiloxane bridged dinuclear compounds. The chemical shifts of the bridgehead carbons in these complexes are about 135 ppm shifted downfield with respect to the other two resonances at cyclopentadienyl ring (113.7 and 113.7 ppm, respectively). In order to investigate the catalytic properties of the dinuclear complexes and mononuclear metallocenes, ethylene polymerisation has been conducted in the presence of MMAO. The most important feature is that the polymethylene bridged dinuclear metallocenes represent enormously improved activities compared with the activities from the corresponding mononuclear metallocene as well as the polysiloxane bridged dinuclear zirconocenes. In addition, the influence of both the nature and length of the bridging ligand upon the reactivities of the dinuclear metallocenes has also been observed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Dinuclear complexes; Distannylated derivatives; Polymethylene bridged dinuclear zirconocenes

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1. Introduction

Group 4 metallocene complexes are of increasing interest in relation to many catalytic reactions, particularly in homogeneous olefin polymerisation [1]. As an advantage over the conventional Ziegler–Natta system, the metallocene catalyst system combines high activity with the possibility of tailoring the polymer properties such as molecular weight and molecular weight distribution as well as stereochemistry through an appropriate ligand design at the metal centre [2].

Recently a variety of dinuclear metallocene compounds, which contain two mechanically linked metallocene units, have been prepared to examine their catalytic properties since dinuclear complexes could be potentially useful as a new polymerisation catalyst ascribed by the cooperative electronic and chemical interaction between two centres. Patterson and Royo prepared a series of dinuclear metallocenes of titanium and zirconium and revealed structural features of these complexes [3]. For the first time, Mülhaupt studied olefin polymerisation behaviours of the phenylene bridged dinuclear zirconocene and demonstrated differences between molecular weights of polypropylenes

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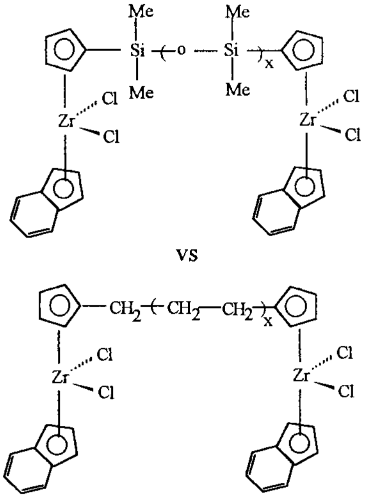
from the dinuclear compound and those from the corresponding mononuclear compound [4]. Recently, Green synthesised a variety of dimethylsilyl-bridged dinuclear metallocenes with Group 4 metals and probed catalytic properties of these complexes [5]. The noticeable feature of his experiments is that the catalytic activities and molecular weight of obtained polymer vary according to the dinuclear metallocene used. In 1997, Corey synthesised a group of dinuclear metallocenes of titanium and zirconium to study catalytic dehydrocoupling of $PhSiH_3$ with the prepared metallocenes and analysed the results in terms of the relative distance between the two metallocene units [6]. More recently, Spaleck and Soga prepared new types of bridged zirconocenes holding two ansa-zirconocenes via bridging silicone atom and examined their polymerisation properties [7]. The first systematic polymerisation study of the dinuclear metallocene was performed by us with the polysiloxane-bridged dinuclear zirconocenes [8]. Our contribution to the dinuclear metallocene area was originated by the idea to design a dinuclear model complex holding polysiloxane moiety in order to explore properties of the heterogenised metallocene on silica surface. Over the last several years we have accomplished not only the synthesis and characterisation of various new types of dinuclear metallocenes, but have also probed the polymerisation behaviour of those compounds. In the case of polysiloxane-bridged dinuclear zirconocenes, it was found that the polymerisation activity increased in the order of the bridge length. In addition, the dinuclear metallocenes possessing relatively shorter bridging ligand, generate greater molecular weight polyethylenes than others. In our understanding these findings clearly demonstrated that the dinuclear metallocenes show not only distinguished properties from the known well-defined mononuclear metallocenes, but also a strong dependence upon the length of the bridging ligand [8a]. Cooperative reactivity pattern of the dinuclear metallocenes may be dependent upon the structure of the bridging ligand as well as the relative distance between two metal centres. This indicates that the nature of the bridging ligand could be the third element to identify the characteristics of dinuclear metallocene together with the metal and cyclopentadienyl derivatives.

On this basis included in this report is a description of the synthesis and characterisations of a family of polymethylene bridged zirconocene complexes of the general formula $[C_5H_4–(CH_2)_n–C_5H_4][Zr(C_7H_9)]_2$ ($n =$ 3, 5, 7, 9) to examine the influence of the types of bridging ligand on the catalytic behaviours of dinuclear metallocene compared with the known polysiloxane bridged complexes. Further, ethylene polymerisation with these complexes in the presence of methylaluminoxane (MAO) is conducted.

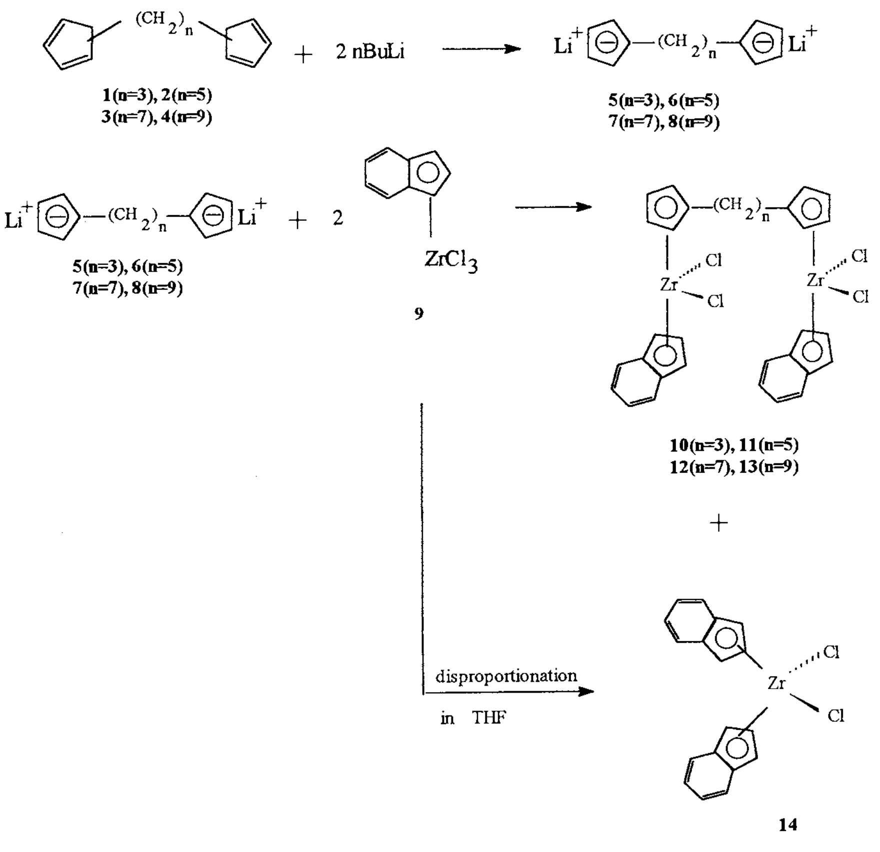


2. Results and discussion

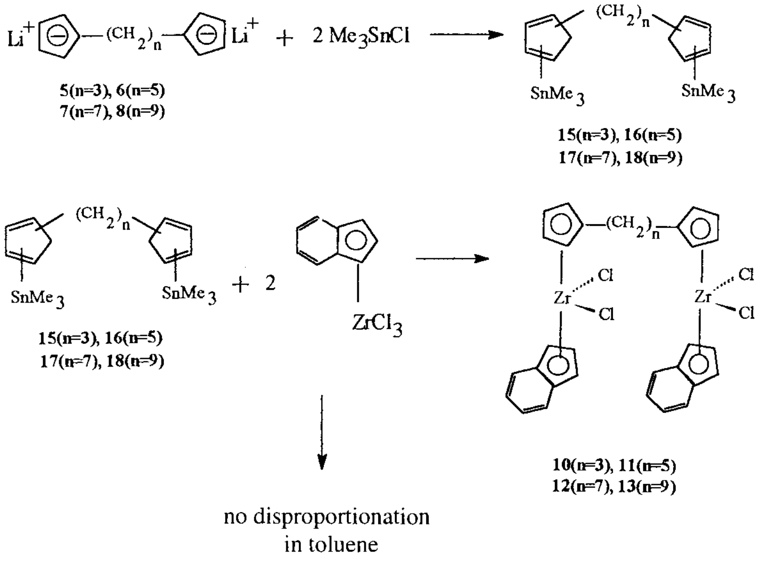
The preparation of the polymethylene bridged dinuclear metallocenes has been achieved via two reaction procedures. Treating the dilithium salts of the ligands **5**–**8** with two equivalents of $(C_9H_7)ZrCl_3$ in THF gives the formation of the respective dinuclear zirconocenes **10**–**13**. The reaction products, however, always contained a considerable amount (about 30%) of $(C_9H_7)_2ZrCl_2$, **14**, along with the desired dinuclear metallocene complexes. In contrast to the polysiloxane bridged dinuclear complexes, the polymethylene bridged dinuclear complexes exhibit very similar solubility property to $(C_9H_7)_2ZrCl_2$. It turned out that sublimation is the only way to get rid of compound **14** from the product mixtures. For this reason, the preparative route to make the dinuclear complexes between the dilithium salts and $(C_9H_7)ZrCl_3$ suffered from the reduced yield of less than 10%. Attempts to prevent the generation of **14** by controlling the reaction conditions were unsuccessful. It was found that generation of **14** was caused by facile rearrangement of $(C_9H_7)ZrCl_3$ to $(C_9H_7)_2ZrCl_2$ in the presence of THF. As a consequence, the dinuclear zirconocenes are invariably produced along with unwanted $(C_9H_7)_2ZrCl_2$ as long as the reaction is performed in THF as a reaction medium. However, the poor solubility of both the dilithium salts and $(C_9H_7)ZrCl_3$ prevents the use of other solvents (Scheme 1).

Recently, Nifant'ev reported that distannylated bis(cyclopentadienes) can be conveniently applied to prepare ansa-metallocenes [9]. We have investigated the performance of his method in the synthesis of dinuclear metallocenes. The expected major advantage of the method using distannylated compounds as one of the starting materials resides in the easy blocking of the rearrangement pathway of $(C_9H_7)ZrCl_3$ to $(C_9H_7)_2ZrCl_2$ due to the solvent substitution from THF to toluene since the distannylated derivatives are soluble in toluene. In a one-pot synthesis, the dilithium salts **5**–**8** were treated with two equivalents of trimethyltin chloride in diethyl ether to give quantitatively distannylated compounds **15**–**18**, respectively, which were then (after removing diethyl ether) reacted with $(C_9H_7)ZrCl_3$ in toluene to give the polymethylene dinuclear zirconocenes **10**–**13**. Remarkably, the products from the reaction do not consist of a variable amount of $(C_9H_7)_2ZrCl_2$ as we had observed in the direct reaction of dilithium salts with $(C_9H_7)ZrCl_3$ in THF. In addition, an added advantage of this route is an easy observation of the reaction progress. During the reaction, disappearance of the starting, insoluble $(C_9H_7)ZrCl_3$ can be seen clearly to give rise to the formation of dinuclear products which are soluble in toluene. Recrystallisation from toluene results in the isolation of polymethylene bridged dinuclear zirconocenes **10**–**13** in improved yields of about 60%, as a bright yellow solid (Scheme 2).

The dinuclear compounds have been characterised by ^{1}H- and ^{13}C-NMR, mass spectrometry, and elemental analysis. ^{1}H-NMR spectra of the complexes **11**–**13** indicate the expected resonances for the bridging polymethylenediylbis(cyclopentadienyl) moiety which appear as two sets of pseudotriplets at 5.92 and 5.82 ppm for **10** and **11** and 5.95 and 5.84 ppm for **12** and **13** with a J_{H-H} value of 2.7 Hz due to an AA′BB′ system and three chemical shifts around 1–2.5 ppm for the methylene protons. The remaining assignments are listed in Table 1. The magnitudes of $\Delta\delta$—the chemical shift difference between the distal and proximal protons on the cyclopentadienyl ring—of the prepared dinuclear zirconocenes display unprecedentedly small values (0.1 for **10** and **11**, 0.11 for **12** and **13**) compared with the known values. In the case of the polysiloxane bridged dinuclear zirconocenes, the magnitudes of $\Delta\delta$ have been reported to increase steadily from 0.47 to 0.5 as the bridging ligand becomes longer [8b]. Although $\Delta\delta$ values of **12** and **13** are slightly bigger than those of **10** and **11**, it is unlikely that this result can be considered as the same tendency as in the case of polysiloxane bridged complexes. One simple interpretation is that the $\Delta\delta$ values appear to be very sensitive to not only the type of free cyclopentadienyl derivative but also the type of bridging ligand. In addition, these could be another example to demonstrate that the $\Delta\delta$ value cannot be employed as an appropriate spectroscopic parameter to predict modes of coordination. Recently Royo mentioned that the chemical shift due to the cyclopentadienyl bridgehead carbon atom of the $[Me_2Si(C_5H_4)_2]^{-2}$ anion seemed to be sensitive to the



Scheme 1.



Scheme 2.

mode of coordination of the ligand [10]. For most dinuclear metallocenes containing this group as a bridging ligand, the chemical shift of the bridgehead carbon is found downfield from the other carbons at the cyclopentadienyl ring, whereas the opposite trend is observed for similar ansa-mononuclear complexes although this spectral feature cannot be applied as a general rule to distinguish the bridging or chelating disposition of the ligand. Very interestingly, this statement has been proved to be very well in accord with the behaviour observed for the dinuclear complexes in this study. The chemical shifts of the bridgehead carbons in these compounds are shown about 135 ppm shifted downfield with respect to the other two resonances (δ 117.3 and 113.7, respectively).

The dinuclear complexes **10**–**13** were employed for the polymerisation of ethylene to investigate the catalytic characteristics in the presence of MMAO ([Al]/Zr ratio of 20 000) at 40°C. The polymerisation activity of the catalysts decreased in the order **13**(5550 kg of PE/mol of Zr h atm) > **12**(4602 kg of PE/mol of Zr h atm) > **11**(3884 kg of PE/mol of Zr h atm) > **10**(2573 kg of PE/mol of Zr h atm). From a standpoint of the catalyst activity there are some important points to be noted to characterise the synthesised complexes. The prime feature is that the activity increases sharply as the bridging ligand becomes longer. This behaviour is very well in accord with the activity tendency observed with the polysiloxane bridged dinuclear zirconocenes [8a]. Fig. 1 displays the relation between the number of atoms in the bridging ligand and activities of the dinuclear zi2rconocenes. It is remarkable that the activity increases steeply and steadily with the number of atoms in the bridging ligand from three methylenes to nine methylenes. The addition of ca. one methylene unit in the bridge exerts 500 kg of PE/mol of Zr h atm on activity among the catalysts **10**–**13**. As shown in Fig. 1, the increasing rate with the polysiloxane bridged catalysts cannot be comparable with that of the polymethylene bridged ones. The second feature is that activity values of the catalysts in this study are much greater than those of the polysiloxane bridged complexes as well as the corresponding mononuclear metallocene $(C_5H_5)(C_9H_7)ZrCl_2$. All the prepared catalysts except **10**, which hold a shortest distance between two zirconocenes, exhibit higher activity than the mononuclear one. On the contrary no catalyst with the polysiloxane bridge represents higher activity than the mononuclear one. Furthermore, the activity difference between two groups of dinuclear zirconocenes is getting larger and larger as the bridge becomes longer.

We think these results can be explained by electronic and steric characteristics of the dinuclear zirconocenes. It is generally accepted that the polymerisation activity of metallocene increases with increasing electron density at the active centre. In our experiments the activity of the catalysts decreased in the order **13** > **12** > **11** > **10**, which indicated the dinuclear zirconocene with more (CH_2) units as a bridge represented greater activity. It is reasonable that the more electron density delivered by the existence of longer polymethylene bridge should stabilise the active site to accelerate the rate of polymerisation. Bimolecular deactivation process could also be suppressed in connected metallocenes because of the remoteness of two active sites [12]. One thing that should be pointed out is the fact that in spite of the presence of the electron releasing polymethylene bridge, the catalyst **10** displays lower activity than the corresponding mononuclear zirconocene which has absolutely no substituent at the Cp ring. We suppose, in this respect, the steric congestion around the zirconium centres will prevail to represent the apparent activity of the dinuclear metallocene and not electronic effect as a consequence of the close distance between two metal centres due to the relatively short bridge length of three (CH_2) units. On the other hand, the dinuclear zirconocenes holding more than five (CH_2) units as a bridge exhibited greater activity than the mononuclear metallocene. This outcome suggests that the length of five (CH_2) units would correspond to the critical distance, that the electronic effect of the bridge in catalytic properties of the dinuclear complexes surpasses the steric hindrance between two metals.

Table 1
Summary of ^1H- and ^{13}C-NMR data[a]

Compound	Assignment	^1H-NMR	^{13}C-NMR
$[(C_5H_4)_2(CH_2)_3][(C_9H_7)ZrCl_2]_2$	C_5H_4	5.92 (t, 2.7)	134.8[b]
		5.82 (t, 2.7)	117.4
		7.66 (m)	126.2
	C_9H_7	7.27 (m)	126.1
		6.90 (t, 3.3)	125.5
		6.50 (d, 3.3)	124.2
	CH_2	2.47 (t, 7.2)	29.4[c]
		1.44 (m)	
$[(C_5H_4)_2(CH_2)_5][(C_9H_7)ZrCl_2]_2$	C_5H_4	5.92 (t,2.7)	135.5[b]
		5.82 (t, 2.7)	117.3
			113.7
	C_9H_7	7.66 (m)	126.2
		7.28 (m)	126.1
		6.90 (t, 3.3)	125.5
		6.49 (d, 3.3)	124.1
			102.7
	CH_2	2.47 (t, 6.6)	29.8
		1.45 (m)	29.7
		1.25 (m)	28.7
$[(C_5H_4)_2(CH_2)_7][(C_9H_7)ZrCl_2]_2$	C_5H_4	5.95 (t,2.7)	135.8[b]
		5.84 (t, 2.7)	117.3
			113.7
	C_9H_7	7.66 (m)	126.1[c]
		7.27 (m)	125.5
		6.90 (t, 3.3)	124.1
	CH_2	2.49 (t, 7.5)	30.3
		1.42 (m)	30.0
		1.21 (br)	29.1
			28.9
$[(C_5H_4)_2(CH_2)_9][(C_9H_7)ZrCl_2]_2$	C_5H_4	5.95 (t, 2.7)	135.8[b]
		5.84 (t, 2.7)	117.3
			113.7
	C_9H_7	7.66 (m)	126.1[c]
		7.27 (m)	125.5
		6.90 (t, 3.3)	124.1
		6.49 (d, 3.3)	102.7
	CH_2	2.49 (t, 7.5)	30.4
		1.43 (m)	30.0
		1.20 (m)	29.3
			29.2[c]

[a] Chemical shifts are in ppm and solvent is $CDCl_3$.
[b] Resonance assigned to bridgehead carbon.
[c] Overlapping of two carbon chemical shifts.

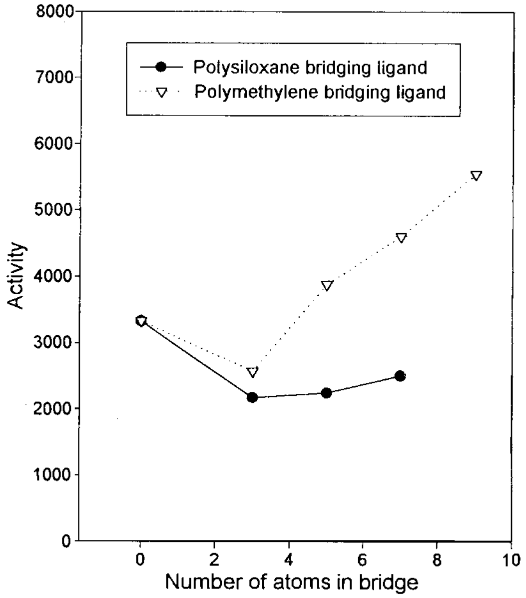
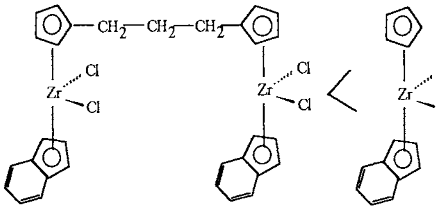
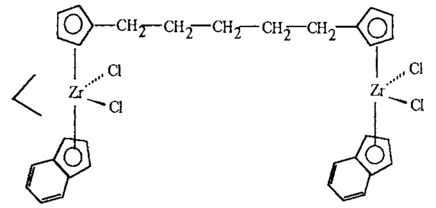


Fig. 1. Variation of activity (kg PE/mol Zr h atm) with the number of atm in bridging ligand. For number of atoms in the bridge = 0, catalyst = (Cp)(ind)$ZrCl_2$. For number of atoms in the bridge = 3, (▽) complex **10**, (●) $[O(SiMe_2C_5H_4)_2][(C_9H_7)ZrCl_2]_2$. For number of atoms in the bridge = 5, (▽) complex **11**, (●) $[O(SiMe_2C_5H_4)_2][(C_9H_7)ZrCl_2]_2$. For number of atoms in the bridge = 7, (▽) complex **12**, (●), $[O\{O(SiMe_2)_2C_5H_4\}_2][(C_9H_7)ZrCl_2]_2$. For number of atoms in the bridge = 9, (▽) complex **13**.



Steric effect > Electronic effect



Steric effect < Electronic effect

3. Summary

The polymethylene bridged dinuclear zirconocenes **10–13** have been synthesised via two procedures. The dinuclear products from the reaction of the dilithium salts of the ligands with $(C_9H_7)ZrCl_3$ was complicated by the accompanying generation of $(C_9H_7)_2ZrCl_2$. However, the route using distannylated derivatives of the ligands instead of the dilithium salts showed a remarkable advantage over the route using lithium salts by the blocking of $(C_9H_7)_2ZrCl_2$ generation. The dinuclear compounds have been characterised by ^{1}H- and ^{13}C-NMR, mass spectrometry, and elemental analysis. The magnitudes of $\Delta\delta$—the chemical shift difference between the distal and proximal protons on cyclopentadienyl ring—of the prepared dinuclear zirconocenes, display unprecedentedly small values (0.1 for **10** and **11**, 0.11 for **12** and **13**) compared with the known values. This result demonstrates that the $\Delta\delta$ values appear to be very sensitive to not only the type of free cyclopentadienyl derivative but also the type of bridging ligand. The chemical shifts of the bridgehead carbons in these compounds are shown about 135 ppm shifted downfield with respect to the other two resonances (δ 117.3 and 113.7, respectively). The dinuclear complexes **10**–**13** were employed in the polymerisation of ethylene to investigate the catalytic characteristics in the presence of MMAO ([Al]/Zr ratio of 20 000) at 40°C. The polymerisation activity of the catalysts decreased in the order **13**(5550 kg of PE/mol of Zr h atm) > **12**(4602 kg of PE/mol of Zr h atm) > **11**(3884 kg of PE/mol of Zr h atm) > **10**(2573 kg of PE/mol of Zr h atm). This indicates that the activity increases sharply as the bridging ligand becomes longer. In addition, all the prepared catalysts except **10**, which hold a shortest distance between two zirconocenes, exhibit higher activity than the mononuclear one as well as the previously reported polysiloxane bridged complexes. These results suggest that the greater electron density delivered by the existence of a longer polymethylene bridge should stabilise the active site to accelerate the rate of polymerisation. In case of the catalyst **10**, the steric congestion around the zirconium centres is more pronounced to represent the activity and not electronic effect as a consequence of the close distance between two metal centres due to the relatively short bridge length of three (CH_2) units. This outcome suggests that the length of five (CH_2) units would correspond to the critical distance that the electronic effect of the bridge is subject to the catalytic properties of the dinuclear complexes over the steric hindrance between two metals.

4. Experimental

All reactions were carried out under a dry, oxygen-free atmosphere using standard Schlenk techniques with a double manifold vacuum line. Nitrogen gas was purified by passage through a column of molecular sieve (4 Å) and Drierite (8 mesh). THF, diethylether, toluene, hexane, and pentane were distilled from sodium/benzophenone ketyl prior to use. Methylene chloride was distilled from phosphorous pentoxide prior to use. White filtering aid (Celite) was stored in a 130°C oven. CpLi, CpNa (2.5 mol solution in THF), and TlOEt were used as purchased from Aldrich. Modified methylaluminoxane (MMAO, Type-4, 6.4 wt.% Al, Akzo, USA) was used without further purification. NMR spectra were recorded at 300 MHz on a Bruker ARX-300 FT-NMR spectrometer. Metal content was measured by Jobin-Yvon 38 Plus ICP Emission Spectrometer. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer between 4000 and 200 cm^{-1}. All the dimetallic salts (indenyl)$ZrCl_3$ were synthesised according to literature methods [3,8,11].

4.1. Synthesis of $[(CH_2)_3C_5H_4)_2][(C_9H_7)ZrCl_2]_2$, **10**

Dilithium 1,3-dicyclopentadienylpropane (0.76 g, 4.08 mmol) was suspended in 50 ml of ether and cooled to −40°C and 1.8 g (9 mmol) of trimethyltin chloride was then added. The resulting mixture was allowed to warm to room temperature and stirred for 5 h. After removal of LiCl by filtration, the solvent was evaporated to give yellow oil (1.9 g, 95%). The distannylated derivative thus obtained was diluted in 50 ml of toluene. Subsequently, 2.60 g of (indenyl)$ZrCl_3$ was added, and the mixture was taken to 80°C and stirred for an additional 6 h. The yellow solution was separated off and the resulting solution was then stored at −70°C to recrystallise the product in 60% yields as a yellow solid.

^{1}H-NMR ($CDCl_3$, 20°C, δ ppm): 7.66 (m, 4H, C_9H_7), 7.27 (m, 4H, C_9H_7), 6.90 (t, 2H, 3.3 Hz, C_9H_7), 6.50 (d, 4H, 3.3 Hz, C_9H_7), 5.92 (t, 4H, 2.7 Hz, C_5H_4), 5.82 (t, 4H, 2.7 Hz, C_5H_4), 2.47 (t, 4H, 7.2 Hz, CH_2), 1.44 (m, 2H, CH_2). ^{13}C-NMR ($CDCl_3$, 20°C, δ ppm): 126.2 (C_9H_7), 126.1 (C_9H_7), 125.5 (C_9H_7), 124.2 (C_9H_7), 102.2 (C_9H_7), 134.8 (C_5H_4), 117.4 (C_5H_4), 113.6 (C_5H_4), 29.4 (CH_2). MS (*m*/*e*): 722 (11, M^+), 607 (70, M^+–Ind), 463 (14, M^+–Ind–Cl_4), 342 (88, (Cp)(Ind)$ZrCl_2$), 170 (39,$(Cp)_2C_3H_6$), 115 (41, Ind).

4.2. Synthesis of $[(CH_2)_5C_5H_4)_2][(C_9H_7)ZrCl_2]_2$, **11**

Dilithium 1,5-dicyclopentadienylpentane (0.88 g, 4.1 mmol) was suspended in 50 ml of ether and cooled to −40°C, and 1.7 g (8.4 mmol) of trimethyltin chloride was then added. The resulting mixture was allowed to warm to room temperature and stirred for 5 h. After removal of LiCl by filtration, the solvent was evaporated to give yellow oil (1.87 g, 95%). The distannylated derivative thus obtained was diluted in 50 ml of toluene. Subsequently, 2.43 g of (indenyl)$ZrCl_3$ was added, and the mixture was taken to 80°C and stirred for an additional 6 h. The yellow solution was separated off and the resulting solution was then stored at − 70°C to recrystallise the product in 60% yields as a yellow solid.

^{1}H-NMR ($CDCl_3$, 20°C, δ ppm): 7.66 (m, 4H, C_9H_7), 7.28 (m, 4H, C_9H_7), 6.90 (t, 2H, 3.3 Hz, C_9H_7), 6.49 (d, 4H, 3.3 Hz, C_9H_7), 5.92 (t, 4H, 2.7 Hz, C_5H_4), 5.82 (t, 4H, 2.7 Hz, C_5H_4), 2.47 (t, 4H, 6.6 Hz, CH_2), 1.45 (m, 4H, CH_2), 1.25 (m, 2H, CH_2). ^{13}C-NMR ($CDCl_3$, 20°C, δ ppm): 126.2 (C_9H_7), 126.1 (C_9H_7), 125.5 (C_9H_7), 124.1 (C_9H_7), 102.7 (C_9H_7), 135.5 (C_5H_4), 117.3 (C_5H_4), 113.7 (C_5H_4), 29.8 (CH_2), 29.7 (CH_2), 28.7 (CH_2). Anal. Found: C, 52.54; H, 4.23. $C_{33}H_{32}Cl_4Zr_2$. Calc.: C, 52.64; H, 4.28%. MS (*m*/*e*): 750 (7, M^+), 680 (10, M^+-Cl_2), 635 (15, M^+−Ind), 490 (15, M^+−Ind−Cl_4), 198 (7, $(Cp)_2C_5H_{10}$), 115 (100, Ind).

4.3. Synthesis of $[(CH_2)_7C_5H_4)_2][(C_9H_7)ZrCl_2]_2$, **12**

Dilithium 1,7-dicyclopentadienylheptane (0.66 g, 2.4 mmol) was suspended in 50 ml of ether and cooled to − 40°C and 1 g (5 mmol) of trimethyltin chloride was then added. The resulting mixture was allowed to warm to room temperature and stirred for 5 h. After removal of LiCl by filtration, the solvent was evaporated to give yellow oil (1.3 g, 95%). The distannylated derivative thus obtained was diluted in 50 ml of toluene. Subsequently, 1.60 g of (indenyl)$ZrCl_3$ was added, and the mixture was taken to 80°C and stirred for an additional 6 h. The yellow solution was separated off and the resulting solution was then stored at − 70°C to recrystallise the product in 60% yields as a yellow solid.

^{1}H-NMR ($CDCl_3$, 20°C, δ ppm): 7.66 (m, 4H, C_9H_7), 7.27 (m, 4H, C_9H_7), 6.90 (t, 2H, 3.3 Hz, C_9H_7), 6.49 (d, 4H, 3.3 Hz, C_9H_7), 5.95 (t, 4H, 2.7 Hz, C_5H_4), 5.84 (t, 4H, 2.7 Hz, C_5H_4), 2.49 (t, 4H, 7.5 Hz, CH_2), 1.42 (m, 4H, CH_2),1.21 (br, 6H, CH_2). ^{13}C-NMR ($CDCl_3$, 20°C, δ ppm): 126.1 (C_9H_7), 125.5 (C_9H_7), 124.1 (C_9H_7). 102.7 (C_9H_7), 135.8 (C_5H_4), 117.3 (C_5H_4), 113.7 (C_5H_4), 30.3 (CH_2), 30.0 (CH_2), 29.1 (CH_2), 28.9 (CH_2). MS (*m*/*e*): 663 (5, M^+−Ind), 511 (5, M^+−Ind−Cl), 342 (5, (Cp)(Ind)$ZrCl_2$), 408 (21, M^+−Ind−Cl_4), 226 (7, $(Cp)_2C_7H_{14}$), 115 (76, Ind).

4.4. Synthesis of $[(CH_2)_9C_5H_4)_2][(C_9H_7)ZrCl_2]_2$, **13**

Dilithium 1,9-dicyclopentadienylnonane (0.8 g, 2.96 mmol) was suspended in 50 ml of ether and cooled to − 40°C, and 1.3 g (6.5 mmol) of trimethyltin chloride was then added. The resulting mixture was allowed to warm to room temperature and stirred for 5 h. After removal of LiCl by filtration, the solvent was evaporated to give yellow oil (1.62 g, 95%). The distannylated derivative thus obtained was diluted in 50 ml of toluene. Subsequently, 1.93 g of (indenyl)$ZrCl_3$ was added, and the mixture was taken to 80°C and stirred for an additional 6 h. The yellow solution was separated off and the resulting solution was then stored at − 70°C to recrystallise the product in 60% yields as a yellow solid.

^{1}H-NMR ($CDCl_3$, 20°C, δ ppm): 7.66 (m, 4H, C_9H_7), 7.27 (m, 4H, C_9H_7), 6.90 (t, 2H, 3.3 Hz, C_9H_7), 6.49 (d, 4H, 3.3 Hz, C_9H_7), 5.95 (t, 4H, 2.7 Hz, C_5H_4), 5.84 (t, 4H, 2.7 Hz, C_5H_4), 2.49 (t, 4H, 7.5 Hz, CH_2), 1.43 (m, 4H, CH_2), 1.20 (m, 10H, CH_2). ^{13}C-NMR ($CDCl_3$, 20°C, δ ppm): 126.1 (C_9H_7), 125.5 (C_9H_7), 124.1 (C_9H_7), 102.7 (C_9H_7), 135.8 (C_5H_4), 117.3 (C_5H_4), 113.7 (C_5H_4), 30.4 (CH_2), 30.0 (CH_2), 29.3 (CH_2), 29.2 (CH_2). Anal. Found: C,54.93; H, 4.98. $C_{37}H_{40}Cl_4Zr_2$. Calc.: C, 54.69; H, 5.36. MS (*m*/*e*): 691 (5, M^+−Ind), 342 (5, (Cp)(Ind)$ZrCl_2$), 254 (3, $(Cp)_2C_9H_{18}$), 115 (43, Ind).

4.5. Polymerisation

All operations were carried out under a nitrogen atmosphere. In a 400 ml glass reactor the proper amount of toluene and MMAO solution were introduced sequentially, and then the system was saturated with ethylene. With continuous flow of ethylene, the polymerisation was initiated by injecting the solution of the prepared dinuclear metallocenes. After 2 h polymerisation, polyethylene was precipitated in acidified methanol.

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