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MMA polymerization with Group 4 alkyl-free 14-electron d⁰ species

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Abstract: Cationic 1,2 and 1,3 doubly-constrained geometry di(silylamido)cyclopentadienyl zirconium complexes, whilst being Group 4 alkyl-free 14-electron d⁰ species, promote the polymerization of MMA. Different cocatalysts such as B(C₆F₅)₃, Al(C₆F₅)₃ and [CPh₃][B(C₆F₅)₄] have been employed to generate the catalytic species in order to collect experimental evidence to propose the polymerization mechanism that these cationic compounds may follow. By systematically studying the role of the active species, this study establishes that the mechanism may be different from the traditional coordination-addition mechanism proposed for group 4 metal complexes in MMA polymerizations.

Introduction

Polymethylmethacrylate (PMMA) is an acrylic polymer with a wide range of applications. The presence of ester groups with a determined tacticity defines its mechanical properties. Moreover, from the environmental point of view, PMMA can be depolymerized affording monomeric MMA in about 100% yield. The synthesis of PMMA can follow different polymerization routes: radical,^[1] ionic,^[1] coordination-addition,^[2] and recently, the frustrated Lewis pair polymerization (LPP)^[3] has also been described. Radical and ionic polymerizations need the presence of a radical or an ionic initiator. However, the coordinationaddition mechanism usually requires the presence of a catalyst;^[2b] with a nucleophilic group that usually initiates the polymerization, as well as an acidic metal centre that coordinates and activates the monomer. Considering chain propagation, a monometallic pathway^[4] is proposed (Figure 1a) when the catalyst has the ability to be both the initiator of the process and the monomer activator, growing the polymer in only one molecule; but a bimetallic pathway is suggested (Figure 1b) when these functions are carried out by two different molecules.^[5-6]



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Figure 1. Intermediates in MMA polymerizations via a monometallic (a) and a bimetallic (b) mechanism.

Moreover, considering the stereocontrol of the polymer, an enantiomorphic site control and a chain end control mechanism can also be proposed. Following the initial studies carried out by Yasuda^[4] and Collins^[5] some reports described that chiral cationic ansa-zirconocene complexes activated with borane afforded highly isotactic PMMA by an enantiomorphic site control mechanism via a monometallic pathway where the anion and the cation are dissociated.^[7-10] However, when activated with alane, the anion and the cation formed ion pairs, the mechanism changed to a chain end pathway producing syndiotactic PMMA *via* a enolaluminate anion by bimetallic propagation as reported by Chen (Figure 2).^[7-10]



Figure 2. Intermediate in MMA polymerizations via in enolaluminates.

A chiral zirconocene cation paired with both, methyl borate and methyl aluminate anions, produced syndiotactic PMMA at 0 °C when the ion pair was formed. However, isotactic PMMA was formed at higher temperatures where the anion and the cation were dissociated.^[9] This proposal is also consistent with the formation of stereomultiblock polymers with iso and sindiotactic domains, where both, the anion and the cation, participate cooperatively in the synthesis of the polymers.^[11] On the other hand, both iso-and syndiotacticity stereoregulation can also be modulated by introducing different substituents in the counteranions.^[12]

In recent years, Stephan and Erker described the concept Frustrated Lewis Pairs (FLP).^[13,14] This frustrated interaction provides these systems with Lewis acidity and basicity available for interaction with a third molecule, even promoting the polymerization of polar monomers as reported by Chen (Figure 3).^[3] Furthermore, considering the nature of the FLP, some efforts have also focused on extending the range of main group Lewis acids to other systems such as cationic early transition metal complexes in the activation of small molecules.^[15-20]

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Figure 3. Intermediate in MMA polymerizations via FLP

Group 4 metallocene and constrained geometry catalysts (CGC) have been widely employed for α -olefins and MMA polymerizations and many efforts have been made to modify the coordination environment of the active species. We reported previously a doubly-silvlamido-bridged cyclopentadienyl group 4 metal complex (Figure 4a) that is an efficient catalyst in the polymerization of α -olefins when activated with MAO, despite generating alkyl-free 14-electron d⁰ cationic species.^[21-23] Similar cationic alkyl-free species to our doubly-silylamido-bridged cyclopentadienyl group 4 metal complexes have been described, for example, the singly silyl-n-amido zirconium dicyclopentadienyl compounds (Figure 4b),^[24] or the amidobridged zirconocene species (Figure 4c),^[25] which also show ethane and methylmethacrylate polymerization activity.



Figure 4. Alkyl-free 14-electron d⁰ group 4 cationic species.

Herein, we report the behavior of 1,2 and 1,3 doubly-constrained geometry di(silylamido)cyclopentadienyl zirconium complexes^[21,26] in the polymerization of MMA using different cocatalysts in order to collect experimental evidence to propose the polymerization mechanism that may follow these cationic species.

Results and Discussion

Generation of the catalytic systems. The precatalysts employed in this study have been synthetized following the different pathways described in the literature by our research group [Zr{ $\eta^5-C_5H_3-1,3-[SiMe_2(\eta^1-NtBu)]$ }R], R=Bz (1),²¹ Me (2)²⁷ and [Zr{ $\eta^5-C_5H_3-1,2-[SiMe_2(\eta^1-NtBu)]$ }Me] (3).^{26a} The reaction of these complexes with B(C₆F₅)₃, Al(C₆F₅)₃ and [CPh₃][B(C₆F₅)₄] proceeds immediately at room temperature affording the corresponding cationic species **4**,²¹ **5**,²³ **6-11** (scheme 1).



Scheme 1. Generation of the catalysts

The ¹H, ¹³C NMR and ¹⁹F NMR spectra of complexes 4-6 in benzene-d₆, at room temperature, show signals consistent with and expected for Cs-symmetric molecules, with two resonances for the cyclopentadienyl (Cp) protons and two resonances for the two nonequivalent methyl groups of the SiMe₂ moieties. The aluminate complexes 7-9 have also been characterized by NMR spectroscopy being also Cs-symmetric molecules. However, complexes 10 and 11, formed by the reaction with $[CPh_3][B(C_6F_5)_4]$, are species with a high ionic character which implies much lower solubility in non-polar deuterated solvents preventing their characterization by NMR. Furthermore, the use of polar solvents to dissolve these derivatives leads to the decomposition of the metal complex. For this reason 10 and 11 could not be characterized by NMR spectroscopy and their characterization is limited. However, based on these experimental observations and the results obtained in the polymerization experiences described below, we suggest that species 10 and 11 should have an identity with the proposed structural disposition described in Scheme 1.

Complexes **1**, **5** and **6** have been characterized by single crystal X-ray diffraction studies (Figures 5-7). The crystallographic details are reported in Table S2. Complexes **1**, **5** and **6** show metal centers with a pseudo-tetrahedral arrangement, these environments are defined by the nitrogen atoms, the Cp group and the benzyl group for complex **1**; or the anionic fragments for **5** and **6**. The values of the angles Cg-Zr-N, close to 100° and smaller by almost 30° than the corresponding angle Cg-Zr-Cg of

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the complex $ZrCp_2Cl_2$,^[28] confirm a constrained geometry for **1**, **5** and **6**. The distances Zr^{...}Me for the ionic complexes **5** and **6** [2.520(4) Å and 2.557(3)] are much longer than the Zr-Me distances observed for the neutral isomers **2**^[26b] and **3**^[26a] [2.318(3) Å and (2.274(2) Å].



Figure 5. ORTEP plot for 1 showing thermal ellipsoids plots.







Figure 7. ORTEP plot for 6 showing thermal ellipsoids plots.

Stability of cationic complexes. Deactivation reactions for these types of complex through the transfer of the C₆F₅ group from the cocatalyst to the metal has been previously described for complexes **4** and **5**.^[23] Herein, we present, before carrying out the polymerization experiments, a comparative study of the stability of all the cationic complexes **4-9** by NMR spectroscopy (scheme 2). Depending on the cocatalyst, the polarity of the solvent or the presence of donor molecules in the reaction mixture, differing stabilities of the cationic species formed have been observed.

First, borate complexes **4-6** have been studied in solution with a non-polar solvent such as benzene-d₆. No evolution at room temperature is observed for **4** and **5**, despite their low solubility. However, compound **6** slowly evolves to complex [Zr{ η 5-C₅H₃-1,2-[SiMe₂(η^1 -N*t*Bu)]}C₆F₅] **12** (Scheme 2). Complexes **4-5** are even thermally stable upon heating these benzene solutions for a few hours up to 80 °C; but on heating over 2 weeks at 80 °C, complexes **4-5** result in the quantitative formation of the 1,3- Zr-

 C_6F_5 complex **A**.^[23] For complex **6**, the C_6F_5 transfer is completed affording complex **12** in only 2 h at 80 °C because of its higher reactivity due to of the higher coordination sphere of 1,2 derivatives.



Scheme 2. Deactivation reaction observed for complexes 4-9.

Second, the behavior of these borate complexes has been studied in the presence of donor ligands. Following Horton criteria^[29] for cationic group 4 complexes with a methyl moiety generated with $B(C_6F_5)_3$, the NMR ¹⁹F spectrum indicates that the ionic species **5** and **6** are contact ion pairs [$\Delta = \delta(F_m - F_p) > 3$] in the absence of donor molecules (Table 1). Nevertheless, the anion-cation interaction is very weak and the addition of a donor ligand, such as pyridine, results in the immediate formation of dissociated ionic pairs [$\Delta = \delta(F_m - F_p) < 3$], as observed for complex 5 (Table 1). However, for the 1,2 di(silylamido) cyclopentadienyl zirconium complex 6, which has a more open coordination site than the 1,3 derivatives, a decomposition of the complex occurs when pyridine is added to the reaction mixture, but when bulkier donor ligands are used, such as CNAr or PPh₃, compound 6 evolves at room temperature to the $Zr-C_6F_5$ complex 12. This process is accelerated by increasing the temperature.

Table 1: ¹⁹F NMR data for complexes 5-6

| Complex | 5 | 5.py | 6 |
|------------------------------|------------|-----------|------------|
| NMR- ¹⁹ F | 132.82 (o) | 131.5 (o) | 133.07 (o) |
| (CeDe) | 158.30 (p) | 164.0 (m) | 158.40 (p) |
| (0606) | 163.61 (m) | 166.5 (p) | 163.68 (m) |
| $\Delta = \delta(F_m - F_p)$ | 5.31 | 2.5 | 5.28 |

In view of these results, we have taken an interest in the use of polar solvents. The study carried out in a more polar solvent such as toluene accelerates the transfer of C_6F_5 in the borate compounds. In benzene, the reaction with **5** needs two weeks at 80 °C to complete the transformation, while in toluene, only 48 h at the same temperature are needed. Using dichloromethane, after ion dissociation, the transfer of chloro is observed affording complexes [Zr{ $\eta^5-C_5H_3-1,3-[SiMe_2(\eta^1-NtBu)]$ CI] **B** and [Zr{ $\eta^5-C_5H_3-1,3-[SiMe_2(\eta^1-NtBu)]$ CI] **C**, which were previously described by our research group by reaction of Li₃[$C_5H_3-1,3-(SiMe_2NtBu)_2$] and ZrCl4.^[26a] Using chloroform as solvent, the formation of **B** and **C** is immediate.

The aluminate complexes **7-9** are less stable in solution than borate complexes. The C_6F_5 transfer process observed for the aluminate species is much faster than that observed for the borate derivatives **5** and **6**. The reaction for the aluminate derivatives **7** and **9** is nearly completed in benzene in two hours at room temperature, while the deactivation reaction for complex **8**, which is more stable, needs 48 hours at room temperature to be completed (Figures S2-S3, supporting information). These reactions are even faster in the presence of donor molecules or at 80°C.^[23]

Polymerization experiments. The polymerization of MMA with complexes **4-11** has been tested at room temperature using toluene as solvent and the results are summarized in Table 2. The 1,3-complexes **4**, **5**, **8** and **10** are very active species (100 h⁻¹ <TOF< 1000 h⁻¹) and the 1,2-complexes **6** and **11** have a moderate activity (10 h⁻¹ <TOF< 100 h⁻¹).^[3] The lower activity of **11** compared to **10** can be explained by the lower reactivity of the Zr-Bz bond with respect to the Zr-Me bond in the initiation reaction. However, aluminate complexes **7** and **9** are inactive in the polymerization of MMA, which may be explained by the rapid transfer of the C₆F₅ group to the metal and the formation of the corresponding inactive pentafluorophenyl complexes **A** and **12**. The GPC analysis for polymers shows a monomodal weight distribution ranging from 1.17 to 1.39.

Table 2. MMA polymerizations promoted by 4-11.

| | | | 1 | | | | |
|-------|-----------------|-------|-------------------|--|--|------------------------------|--------------------|
| Entry | Cat | t (h) | conv ^b | TOF (h ⁻¹) ^c | 10 ⁴ Mn (exp) ^c | 10⁴ Mw (exp) ^c | PDI ^{c,d} |
| 1 | 4 | 0.5 | 95 | 235 | 8.72 | 10.95 | 1.25 |
| 2 | 5 | 0.5 | 59 | 125 | 5.79 | 7.70 | 1.33 |
| 3 | 3 | 2 | 93 | 49 | 7.10 | 8.73 | 1.23 |
| 4 | 6 | 0.5 | 16 | 34 | 1.38 | 1.66 | 1.21 |
| 5 | 0 | 2 | 25 | 13 | 2.41 | 2.83 | 1.17 |
| 6 | 7 | 0.5 | 0 | - | - | - | - |
| 7 | ' | 2 | 0 | - | - | - | - |
| 8 | 0 | 0.5 | 47 | 100 | 4.25 | 5.61 | 1.32 |
| 9 | 0 | 2 | 92 | 49 | 6.72 | 9.39 | 1.39 |
| 10 | 9 | 2 | 0 | - | - | - | - |
| 11 | 10 ^e | 0.5 | 95 | 235 | 6.64 | 8.66 | 1.30 |
| 12 | 10 ^f | 0.5 | 92 | 188 | 6.80 | 8.71 | 1.28 |
| 13 | | 2 | 96 | 51 | 4.78 | 5.81 | 1.21 |
| 14 | 11 | 0.5 | 4 | 8 | 1.66 | 1.93 | 1.16 |
| 15 | | 2 | 12 | 6 | 2.25 | 3.00 | 1.33 |

a) General conditions: toluene (4 mL), precatalysts (40 μ mol), MMA (1 g), T= 25 °C, (monomer) / (initiator) molar ratio=250:1, precipitation of PMMA with 100 mL of MeOH. b) conv.= (polymer mass / used monomer mass). c) Calculated by GPC with polystyrene standards. d) PDI=Mw/Mn. e) Generated from 1. f) Generated from 2.

All the PMMA samples obtained have a similar tacticity, being predominantly syndiotactic with an abundance of the rr triad between 59 and 65 % in all cases (Table 3). A triad analysis^[30] is a simple method to calculate the stereocontrol mechanism of the polymerization; a relation in the triads 2[rr]/[mr] close to 1 indicates enantiomorphic site control while a relation 4[mm][rr]/[mr]² close to 1 corresponds to a chain end control mechanism. The data collected in table 3 show that the polymer chain-end controls the syndiospecificity of the polymers.

Table 3: Triad analysis and stereocontrol mechanism

| | Cat | conv ^a | t (h) | Triads ^b (rr, mr, mm) | 2[rr]/ [mr] | 4[mm] [rr]/[mr] ² | l(%) ^e |
|----|-----------------|-------------------|-------|--|----------------|---------------------------------|-------------------|
| 1 | 4 | 95 | 0.5 | 65:32:3 | 4.06 | 0.76 | 13.6 |
| 3 | 5 | 93 | 2 | 59:33:8 | 3.57 | 1.73 | 13.9 |
| 5 | 6 | 25 | 2 | 60:36:4 | 3.33 | 0.74 | 11.2 |
| 9 | 8 | 92 | 2 | 63:34:3 | 3.70 | 0.65 | 14.6 |
| 11 | 10 ^f | 95 | 0.5 | 62:35:3 | 3.54 | 0.61 | 17.9 |
| 13 | 10 ^g | 96 | 2 | 62:34:4 | 3.64 | 0.86 | 21.5 |
| 15 | 11 | 12 | 2 | 62:33:5 | 3.75 | 1.13 | 5.8 |

a) conv.= (polymer mass / used monomer mass) x 100. b) Tacticity determined by ¹H NMR in CDCl₃. c) Enantiomorphic site control mechanism: 2[rr]/[mr]= 1. d) Chain end control mechanism: $4[mm][rr]/[mr]^2 = 1.$ e) l= (Mn (calc)/ Mn (exp)) x 100. f) Generated from 1. g) Generated from 2.

The molecular weights obtained are higher than expected. Despite the high conversion values in the MMA polymerization with **4**, **5**, **8** and **10**, only <15% of the Zr catalyst is productive indicating that a deactivation of the active species occurs in the catalytic process (Table 3, I), probably explained by the alreadymentioned C_6F_5 transfer from the anion to the cation.

The MALDI mass spectrum (Figure S7, supporting information) using DCTB as matrix and Nal as ionizating agent of all the analyzed PMMA samples (entries 1, 9, 11, 15, table 2) show a series of peaks (909, 1009, 1109, 1209...) corresponding to a repeat unit of MMA, but these peaks are shifted to -16 Da to the standard PMMA [M+Na]⁺, which could fit with terminals H (1 Da) and methyl acrylate group (85 Da), instead of methyl methacrylate (100 Da), by lost of CH₄ (-16 Da); [M+Na]⁺ = [(MMA)_n+85+23+1].

Mechanistic considerations: We have taken a particular interest in obtaining conclusions from the results described above about the catalytic activity of complexes **4-11** with respect the reaction pathways in these catalytic processes. For this purpose, it is interesting to stablish a comparative study between the data previously described in this paper and the polymerization mechanisms reported in the literature for similar systems.^[24-25, 31-32]

Alkyl free cationic group 4 metal complexes described in the literature similar to our metal derivatives (Figure 4) are only active in the MMA polymerization under certain reaction conditions. The singly silyl-η-amido zirconium dicyclopentadienyl complexes described by Chen et al^[24] does not polymerize MMA when activated with 1 eq of B(C₆F₅)₃, but when it is activated with Al(C₆F₅)₃, an efficient catalyst is formed. The authors propose that the reaction probably follows a pathway via enolaluminate intermediates (Figure 2).^[7] The amido double-bridged zirconocene species described by Wang et al^[25] is not active either in the presence of 1 eq of B(C₆F₅)₃, but when 0.5 eq of B(C₆F₅)₃ are used, syndiotactic PMMA is formed because together with the cation complex necessary to activate the monomer, the neutral species is needed to initiate the process.

Therefore, in this case, a bimetallic mechanism^[5] must be the reaction pathway (Figure 1b).

The polymerization experiments carried out with our cationic doubly-silylamido-bridged cyclopentadienyl complexes (Tables 2 and 3) afford some experimental evidence that permits us to draw some conclusions:

a) The triad analysis shows that the polymer chain-end controls the syndiospecificity of the polymers (Table 3).

b) The conversion of MMA is maximum when 1 eq of $B(C_6F_5)_3$ is used (Table 4). In this process the coexistence of the neutral and the cationic species to get a catalytically active system is not necessary. This behavior rules out the bimetallic polymerization mechanism described by Collins (Figure 1b).^[5]

Table 4: MMA polymerizations with 1 and different molar ratio of $B(C_6F_5)_3$

| 1 0.25 60 38 64: 33: 3 2 0.50 60 84 63: 32: 5 2 0.75 20 90 65: 20: 5 | Entry ^a | B(C ₆ F ₅) ₃ ^b | t (min) | conv (%) ^c | (rr: mr: mm) ^d |
|--|--------------------|---|---------|-----------------------|---------------------------|
| 2 0.50 60 84 63: 32: 5 2 0.75 20 00 65: 30:5 | 1 | 0.25 | 60 | 38 | 64: 33: 3 |
| 2 0.75 20 00 65:20:5 | 2 | 0.50 | 60 | 84 | 63: 32: 5 |
| 3 0.75 30 90 05.30.5 | 3 | 0.75 | 30 | 90 | 65: 30:5 |
| 4 1 30 92 63: 32: 5 | 4 | 1 | 30 | 92 | 63: 32: 5 |

a) 40 μ mol of precatalyst, T= 25 °C, toluene (4 mL), MMA (1 g), (monomer) / (initiator) molar ratio=250:1, precipitation of PMMA with 100 mL of MeOH, b) Equiv of cocatalyst, c) % conv= (g of PMMA/ g of MMA) x 100, d) triads relation determined by ¹H-NMR in CDCl₃.

c) The cationic doubly-silylamido-bridged cyclopentadienyl zirconium complexes which are rapidly deactivated by transfer of C_6F_5 are the least active species in the catalytic process. For compounds **7** and **9** this transfer process is very fast justifying their inactivity in the MMA polymerization. On the other hand, the dissociated ionic complexes **4** and **10** are the most active species in the polymerization reaction (Table 2), indicating the importance of the ionic character in its catalytic behavior.

d) In order to study the influence of the anionic moiety, $Al(C_6F_5)_3$ and $[CPh_3][B(C_6F_5)_4]$ have also been used as cocatalysts. The conclusion is that the uses of different cocatalysts do not affect the triad's relation and the polymer's properties. Even the use of a large excess of $Al(C_6F_5)_3$ does not affect the microstructure of the resulting polymers, the catalytic activities or the reaction rate (Table 3). These results rule out polymerization pathways with an enoaluminate active species described by Chen (Figure 2)^[7-10] in all polymerizations carried out with alane.

e) Recent studies with classical acid-base aducts (CLA) and FLP conclude that CLA can perform with high polymerization activity if they are frustrated in solution. However, if the CLA does not dissociate even in solution, no polymerization is observed.^[33] In our case, the ionic pairs have been studied in

solution and a dissociation of the ion pair is observed (e.g. **5-py**). Therefore, our system could polymerize MMA through a pathway reaction that implies, in the presence of the monomer, the participation of FLP as an intermediate (Figure 3).

f) Frustrated Lewis Pairs are usually described as nonclassical Lewis pairs including bulky Lewis Acids like $B(C_6F_5)_3$ or $Al(C_6F_5)_3$, and bulky Lewis Bases like phosphines or carbenes, in which steric hindrance avoids the formation of stable classical aducts. However, some efforts have also focused on extending the range of main group Lewis acids to other systems such as cationic early transition metal complexes in the activation of small molecules.^[15-20] In our case, the cationic zirconium complex could act as the LA and the corresponding anion as the LB (Figure 8).



Figure 8. Proposed intermediate species in MMA polymerization with di(silylamido)cyclopentadienyl zirconium complexes.

g) In a typical FLP, a high interaction between the LA and the LB produces chain termination side reactions due to LA-activated backbiting cyclization.^[34] This side reaction is not observed in our polymerization studies because our ion pairs are dissociated in solution.

Conclusions

In view of all described experimental observations and all the analyzed results we conclude that the Group 4 alkyl-free 14electron d⁰ complexes studied here, in the MMA polymerization, do not follow the previously proposed mechanisms for other alkyl-free 14-electron d⁰ group 4 cationic species involving a monometallic or a bimetallic intermediates, as depicted in Figure 1, nor enolaluminates species (Figure 2). A reaction pathway involving ion-pair species, or even a FLP pathway could be more faithful to justify the results obtained in our research.

Experimental Section

Experimental section: All manipulations were performed under an inert atmosphere using standard Schlenk-line techniques ($O_2 < 3ppm$) and MBraun MB-20G glovebox ($O_2 < 0.6 ppm$). Solvents were dried by conventional procedures and freshly distilled prior to use. Deuterated solvents were degassed by freeze-vacuum-thaw cycles and stored in

the glovebox in the presence of molecular sieves (4 Å). B(C₆F₅)₃,³⁵ Ph₃CB(C₆F₅)₄,³⁶ and (0.5 toluene)Al(C₆F₅)₃,³⁷ were prepared according to the literature. Methylmethacrylate was dried overnight with CaH₂ and distilled twice under vacuum. It was stored in the absence of light at -20°C for very short periods of time.

NMR spectra were recorded with a Bruker 400 Advance Ultrashield (¹H 400.13 MHz, ¹³C 100.6 MHz and ¹⁹F 376.70 MHz). All chemical shifts were determinated using the residual signal of solvents and were reported versus SiMe₄. MALDI-TOF analysis was performed using a ULTRAFLEX III, DCTB was used as matrix and Nal as ionizating agent. Due to the air and moisture sensitivity of the cationic group 4 metal complexes, elemental analysis experiments were unsuccessful. Despite its low solubility in non-polar solvents, and in order to avoid the fast decomposition of the cationic complexes, the characterization of the precatalysts was carried out in C₆D₆.

Formation of complexes {[Zr{ $\eta^{5}-C_{5}H_{3}-1,3-[SiMe_{2}(\eta^{1}-NtBu)]_{2})$][RB(C₆F₅)₃]}, R=Bn (4) and Me (5), {[Zr{ $\eta^{5}-C_{5}H_{3}-1,2-[SiMe_{2}(\eta^{1}-NtBu)]_{2}$ }][MeB(C₆F₅)₃]} (6)

The cationic species 4, 5 and 6 were generated in a teflon valved NMR tube by the reaction of the corresponding alkyl complexes 1, 2 or 3 (20 $\mu mol)$ with the cocatalyst $B(C_6F_5)_3$ in a molar ratio 1:1. The reaction proceeds immediately and quantitatively at room temperature.

$$\begin{split} & \{ [Zr\{\eta^5-C_5H_3-1,3-[SiMe_2(\eta^1-NtBu)]_2\}] [BnB(C_6F_5)_3] \} \ (4). \ ^{1}H \ NMR \ (C_6D_6, 295 \\ K, \ 400.13 \ MHz): \ \delta = \ 6.91 \ (m, \ 2H, \ C_6H_5), \ 6.40 \ (m, \ 2H, \ C_6H_5), \ 6.16 \ (m, \ 1H, \\ C_6H_5), \ 6.02 \ (m, \ 1H, \ C_5H_3), \ 5.23 \ (m, \ 2H, \ C_5H_3), \ 3.44 \ (s, \ 2H, \ CH_2), \ 1.02 \ (s, \\ 18H, \ NtBu), \ 0.38 \ (s, \ 6H, \ SiCH_3), \ 0.20 \ (s, \ 6H, \ SiCH_3). \ ^{13}C \ NMR \ (C_6D_6, \\ 295 \ K, \ 100.6 \ MHz): \ \delta = \ 162.0 \ (C_6H_5), \ 149.8 \ (C_6F_5), \ 147.8 \ (C_6F_5), \ 138.3 \ (C_6F_5), \ 128.3 \ (C_6H_5), \ 128.1 \ (C_6H_5), \ 127.4 \ (C_5H_3), \ 123.5 \ (C_5H_3), \ 121.4 \ (C_5H_3), \ 58.6 \ (NtBu), \ 34.8 \ (NtBu), \ 1.6 \ (SiMe_2), \\ 1.5 \ (SiMe_2). \ ^{19}F \ NMR \ (C_6D_6, \ 295 \ K, \ 376.70 \ MHz): \ \delta = \ 167.2 \ (m, \ 2F, \ m-C_6F_5), \ 132.1 \ (m, \ 2F, \ o-C_6F_5). \end{split}$$

 $\label{eq:constraint} \begin{array}{l} \{ [Zr\{\eta^5-C_5H_3-1,3-[SiMe_2(\eta^1-NtBu)]_2\}] [MeB(C_6F_5)_3] \} \ \ (\textbf{5}). \ \ ^1H \ \ NMR \ \ (C_6D_6, \\ 295 \ \ K, \ 400.13 \ \ MHz): \ \delta = \ 6.48 \ \ (m, \ 2H, \ \ C_5H_3), \ 6.31 \ \ (m, \ 1H, \ \ C_5H_3), \ 0.94 \ \ (s, \\ 18H, \ \ NtBu), \ 0.91 \ \ (s, 3H, \ BCH_3), \ 0.33 \ \ (s, \ 6H, \ SiCH_3), \ 0.21 \ \ (s, \ 6H, \ SiCH_3), \\ 18H, \ \ NtBu), \ 0.91 \ \ (s, 3H, \ BCH_3), \ 0.33 \ \ (s, \ 6H, \ SiCH_3), \ 0.21 \ \ (s, \ 6H, \ SiCH_3), \\ 18H, \ \ NtBu), \ 0.91 \ \ (s, 3H, \ BCH_3), \ 0.33 \ \ (s, \ 6H, \ SiCH_3), \ 0.21 \ \ (s, \ 6H, \ SiCH_3), \\ 18H, \ \ NtBu), \ 0.91 \ \ (s, 3H, \ BCH_3), \ 0.33 \ \ (s, \ 6H, \ SiCH_3), \ 0.21 \ \ (s, \ 6H, \ SiCH_3), \\ 18H, \ \ NtBu), \ 0.91 \ \ (s, \ 6H, \ SiCH_3), \ 0.21 \ \ (s, \ 6H, \ SiCH_3), \\ 18H, \ \ NtBu), \ 0.91 \ \ (s, \ 6H, \ SiCH_3), \ 0.21 \ \ (s, \ 6H, \ SiCH_3), \ 0.21 \ \ (s, \ 6H, \ SiCH_3), \ 0.21 \ (s, \ 6H, \ SiCH_3), \ 0.21 \ \ (s, \ 6H, \ SiCH_3), \ 0.21 \ \ (s, \ 6H, \ SiCH_3), \ 0.21 \ \ (s, \ 6H, \ SiCH_3), \ 0.21 \ \ (s, \ 6H, \ SiCH_3), \ (s, \ 6H, \ (s, \ 6H, \ SiCH_3), \ (s, \ 6H, \ SiCH_3), \ (s, \ 6H, \ SiCH_3), \ (s, \ 6H, \ (s, \ 6H, \ (s, \ 6H, \ 6H, \ (s, \ 6H, \ (s, \ 6H, \ 6H, \ (s, \$

| Formation | of | complexes | {[Zr{η ⁵ -C ₅ H ₃ -1,3-[SiMe ₂ (η ¹ - |
|----------------|---|-----------|--|
| NtBu)]2}][BnA | I(C ₆ F ₅) ₃]} | (7), | {[Zr{η ⁵ -C ₅ H ₃ -1,3-[SiMe ₂ (η ¹ - |
| NtBu)]2}][MeA | $I(C_6F_5)_3]$ | (8), | {[Zr{η ⁵ -C ₅ H ₃ -1,2-[SiMe ₂ (η ¹ - |
| NtBu)]_}][AI(C | F_{5}]3]} (9). | | |

The cationic species **7**, **8** and **9** were generated by the reaction of the corresponding alkyl complexes **1**, **2** or **3** (20 µmol) with the cocatalyst Al(C₆F₅)₃ in a molar ratio 1:1, the reaction proceeds immediately and quantitatively at room temperature. Evolution in solution to the [Zr]-C₆F₅ species did not permit proper ¹³C-NMR spectra of **7-9** to be recorded.

 $\begin{array}{l} \{ [Zr\{\eta^5-C_5H_3-1,3-[SiMe_2(\eta^1-NtBu)]_2\}] [BnAl(C_6F_5)_3] \} \ \ (7). \ \ ^1H \ \ NMR \ \ (C_6D_6, \\ 295 \ \ K, \ 400.13 \ \ MHz): \ \ \delta=7.20-6.83 \ \ (m, \ 5H, \ C_6H_5), \ 6.52 \ \ (m, \ 2H, \ C_5H_3), \\ 6.11 \ \ (m, \ 1H, \ C_5H_3), \ 2.80 \ \ (s, \ 2H, \ CH_2), \ 1.02 \ \ (s, \ 18H, \ NtBu), \ 0.29 \ \ (s, \ 6H, \\ SiCH_3), \ 0.21 \ \ (s, \ 6H, \ SiCH_3). \ \ ^{19}F \ \ NMR \ \ (C_6D_6, \ 295 \ \ K, \ 376.70 \ MHz): \ \ \delta=162.5 \ \ (m, \ 2F, \ m-C_6F_5), \ 155.6 \ \ (m, \ 1F, \ p-C_6F_5), \ 120.8 \ \ (m, \ 2F, \ o-C_6F_5). \end{array}$

 $\label{eq:constraint} \begin{array}{l} \{ [Zr\{\eta^5-C_5H_3-1,3-[SiMe_2(\eta^1-NtBu)]_2\}] [MeAl(C_6F_5)_3] \} \ \ (\textbf{8}). \ \ ^1H \ \ NMR \ \ (C_6D_6, 295 \ K, 400.13 \ MHz): \ \delta= 6.53 \ (m, 2H, \ C_5H_3), 6.34 \ (m, 1H, \ C_5H_3), 0.99 \ (s, 18H, \ NtBu), 0.45 \ (s, 3H, \ Me), 0.32 \ (s, 6H, \ SiCH_3), 0.24 \ (s, 6H, \ SiCH_3). \end{array}$

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 ^{19}F NMR (C₆D₆, 295 K, 376.70 MHz): $\delta =$ 161.5 (m, 2F, m-C₆F₅), 153.6 (m, 1F, p-C₆F₅), 122.7 (m, 2F, o-C₆F₅).

Formation of $[Zr{\eta^5-C_5H_{3}-1,2-[SiMe_2(\eta^1-NtBu)]}C_6F_5]$ (12). Complexes 6 and 9 in solution evolve to 12, even in benzene-d₆ solutions.

 $\begin{array}{l} \{ [Zr\{\eta^5-C_5H_3-1,2-[SiMe_2(\eta^1-NtBu)]\}C_6F_5] \} \ (12). \ ^{1}H \ \ \text{NMR} \ \ (C_6D_6, \ 295 \ \ \text{K}, \\ 400.13 \ \ \text{MHz}): \ \delta = \ 6.79 \ (m, \ 3H, \ \ C_6H_5), \ 1.30 \ (s, \ 18H, \ \ NtBu), \ 0.51 \ (s, \ 6H, \\ SiCH_3), \ 0.48 \ (s, \ 6H, \ \ SiCH_3). \ ^{13}C \ \ \text{NMR} \ \ (C_6D_6, \ 295 \ \ \text{K}, \ 100.6 \ \ \text{MHz}): \ \delta = \\ 150.1 \ \ (C_6F_5), \ 147.8 \ \ (C_6F_5), \ 139.3 \ \ (C_6F_5), \ 135.9 \ \ (C_6F_5), \ 131.3 \ \ (C_5H_3), \\ 128.2 \ \ (C_5H_3), \ 117.2 \ \ (C_5H_3), \ 57.4 \ \ (NtBu), \ 34.7 \ \ (NtBu), \ 5.2 \ \ (SiMe_2), \ 2.9 \ \ (SiMe_2). \ ^{19}F \ \ \text{NMR} \ \ (C_6D_6, \ 295 \ \ \text{K}, \ 376.70 \ \ \text{MHz}): \ \delta = \\ 160.9 \ \ (m, \ 2F, \ m-C_6F_5), \ 135.6 \ \ (m, \ 1F, \ p-C_6F_5), \ 116.1 \ \ (m, \ 2F, \ o-C_6F_5). \end{array}$

Methyl methacrylate polymerization. The MMA polymerization runs were carried out inside of the dry box, at room temperature, in topaz glass vials equipped with a magnetic stirrer and following a standard procedure. $4x10^{-5}$ mol the precatalyst, the appropriate amount of the desired cocatalyst and 4 ml of toluene were added to the reactor in that sequence. The reaction mixture was stirred for 1 minute and 1 ml of MMA was added. The polymerization reactor was taken out after the prescribed time and the process was stopped by adding a few milliliters of acidic methanol. The mixture was precipitated in 50 mL of methanol and recovered by filtration. The purification of the polymer was carried out by recrystallization from a saturated solution of PMMA in acetone which is precipitated in cold methanol. The recrystallized polymer was filtered again and dried under vacuum at 50 ° C to constant weight.

Single Crystal X-ray diffraction of 1, 5.0.5C6H6 and 6.C6H6. Data collection was performed at 200(2) K or 150(2) K, with the crystals covered with perfluorinated ether oil. Single crystals of 1, 5-0.5C₆H₆ and 6-C6H6 were mounted on a Bruker-Nonius Kappa CCD single crystal diffractometer equipped with a graphite-monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å). Multiscan³⁸ absorption correction procedures were applied to the data. The structure was solved using the WINGX package,³⁹ by direct methods (SHELXS-13) and refined using full-matrix least-squares against F² (SHELXL-16).⁴⁰ All non-hydrogen atoms were anisotropically refined except for two tBu groups in 1 and 5 that showed positional disorder that was treated, and the atoms left isotropic. Hydrogen atoms were geometrically placed and left riding on their parent atoms, except for the hydrogens bonded to C13 in compound 1 and C10 in compounds 5 and 6, which were found in the Fourier map and refined freely. For compound 6, one molecule of solvent crystalized for every molecule, this molecule shows some disorder, but it was not treated. Fullmatrix least-squares refinements were carried out by minimizing $\sum w(Fo^2)$ $-Fc^{2}$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1917000 [1], CCDC-1917001 [5-0.5C6H6] and CCDC-1917002 [6· C₆H₆].

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Keywords: zirconium • polymerization • MMA • FLP • mechanism

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Entry for the Table of Contents

FULL PAPER



Doubly-silylamido-bridged cyclopentadienyl group 4 metal complexes can polymerize MMA through a pathway reaction that does not match with other previously proposed mechanisms for analogous alkyl-free 14-electron d⁰ group 4 cationic species. Probably the participation of ion-pairs or FLP, as intermediates, could be considered.

MMA polymerization mechanisms

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MMA polymerization with Group 4 alkyl-free 14-electron d⁰ species