Synthesis of Neutral and Cationic Monocyclopentadienyl Tantalum Alkoxo Complexes and Polymerization of Methyl Methacrylate

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Received February 23, 2007

The alkoxo compounds [TaCp*Me$_3$(OR)] (R = Si*i*Pr$_3$, **1a**; 2,6-Me$_2$C$_6$H$_3$, **1b**; 2,6-*i*Pr$_2$C$_6$H$_3$, **1c**) were obtained by reaction of [TaCp*Me$_4$] with the corresponding alcohol ROH, at room temperature for R = Si*i*Pr$_3$ and upon heating at 100 °C over 2 and 3 days for R = 2,6-Me$_2$C$_6$H$_3$ and 2,6-*i*Pr$_2$C$_6$H$_3$, respectively. The alkoxo cations [TaCp*Me$_2$(OR)]$^+$ (R = Si*i*Pr$_3$, **2a**; 2,6-Me$_2$C$_6$H$_3$, **2b**; 2,6-*i*Pr$_2$C$_6$H$_3$, **2c**) were formed when one of the methyl groups of the neutral trimethyl complexes **1** was dissociated by reaction with 1 equiv of B(C$_6$F$_5$)$_3$ to generate the borate anion [MeB(C$_6$F$_5$)$_3$]$^-$ (**B**) and with 1 and 2 equiv of Al(C$_6$F$_5$)$_3$ to give the mononuclear [MeAl(C$_6$F$_5$)$_3$]$^-$ (**Al**) and dinuclear [Me{Al(C$_6$F$_5$)$_3$}$_2$]$^-$ (**Al2**) aluminate anions, respectively. A similar reaction of the neutral compound [TaCp*Me$_4$] with 1 and 2 equiv of Al(C$_6$F$_5$)$_3$ gave salts of the [MeAl(C$_6$F$_5$)$_3$]$^-$ (**Al**) and [Me{Al(C$_6$F$_5$)$_3$}$_2$]$^-$ (**Al2**) anions containing the [TaCp*Me$_3$]$^+$ (**3**) cation. Compounds **1** and [TaCp*Me$_4$] did not show catalytic activity for MMA polymerization when B(C$_6$F$_5$)$_3$ was used as cocatalyst but were active in the presence of Al(C$_6$F$_5$)$_3$, yielding high molecular weight syndiotactic PMMA.

Introduction

The polymerization of methacrylates by transition metal complexes is receiving growing attention in relation to the control of the stereochemistry and polydispersity of the polymer chain and the production of well-defined block copolymers.[1−7] The stereoregulation of the polymethylmethacrylate (PMMA) depends not only on the nature of the transition metal complex but also on the cocatalyst. Thus, cationic zirconocene enolates are the propagating species when zirconocenium borate complexes are used as catalysts, producing isotactic PMMA,[8−13] whereas anionic enolaluminates were the active species when zirconocenium aluminate derivatives were used as catalysts to give syndiotactic PMMA.[14,15] Both processes proceeded through a bimetallic mechanism, whereas a straightforward mononuclear group transfer mechanism (GTP) was proposed for samarocene complexes.[4]

Methyl methacrylate (MMA) polymerization with lanthanocenes and group 4 metallocene complexes has been widely explored in the last few years,[3,16−20] and recently, Chen and co-workers have extended this application to group 5 metallocene derivatives,[21,22] taking into account that they should show a more tolerant attitude toward this type of polar olefin than the more electron-deficient analogues of the lanthanides and group 4 metal derivatives. The catalysts based on [TaCp$_2$Me$_3$]/2Al(C$_6$F$_5$)$_3$[21] and [TaCp$_2$(CH$_2$)Me]/2Al(C$_6$F$_5$)$_3$[22] systems gave syndiotactic PMMA of high molecular weight ($M_n > 10^5$), with narrower polydispersity for the alkylidene derivative [TaCp$_2$(CH$_2$)Me], both proceeding through a bimolecular anionic enolaluminate mechanism. In addition, Yashuda et al. reported that the monocyclopentadienyl tantalum compound [TaCp*(DAD)(MMA)] (DAD = N(R)CH═CHN(R)), with coordinated η^4-MMA, also produced syndiotactic PMMA when activated with AlMe$_3$ in a living fashion.[23]

In previous work, we isolated the ionic monocyclopentadienyl tantalum compound [TaCp*Me$_3$][MeB(C$_6$F$_5$)$_3$], which showed rather poor activity as an ethylene polymerization catalyst.[24] Following our research on monocyclopentadienyl tantalum cationic complexes we report here the synthesis of new neutral monoalkoxo derivatives [TaCp*Me$_3$(OR)], their reactions with

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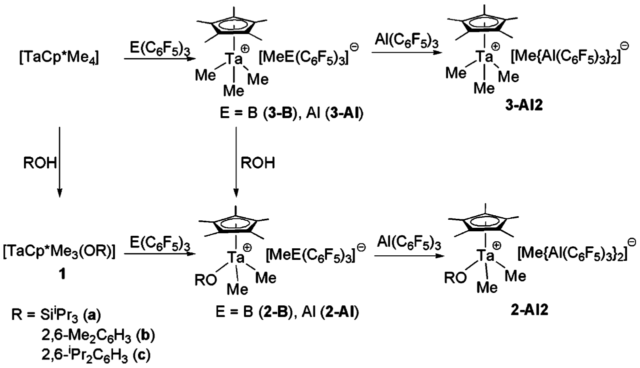
10.1021/om070166+ CCC: $37.00

Scheme 1



the Lewis acids $E(C_6F_5)_3$ (E = B, Al), and the reaction of $[TaCp^*Me_4]$ with $Al(C_6F_5)_3$. We also report the applications of all these systems as suitable catalysts for MMA polymerization.

Results and Discussion

Synthesis of Alkoxo Compounds. We were interested in extending our studies on the successful controlled hydrolysis of $[TaCp^*Me_4]$[25] and decided to explore the protonolysis reactions of the title compound with different alcohols ROH (R = Si*i*Pr$_3$, 2,6-$Me_2C_6H_3$, 2,6-*i*$Pr_2C_6H_3$) with the aim of isolating new monoalkoxo derivatives. Hence, the monoalkoxo complexes $[TaCp^*Me_3(OR)]$ (R = Si*i*Pr$_3$, **1a**; 2,6-$Me_2C_6H_3$, **1b**; 2,6-*i*$Pr_2C_6H_3$, **1c**) were obtained as yellow solids very soluble in common solvents from reaction of $[TaCp^*Me_4]$ with ROH in toluene (Scheme 1). The reaction with the most acidic alcohol *i*Pr_3SiOH, due to the presence of the electron acceptor silicon atom, proceeded easily at room temperature to give the siloxo derivative **1a**, whereas much slower reactions were observed for the less acidic phenol derivatives. Both required heating at 100 °C, although reaction was complete for the less sterically demanding alcohol (R = 2,6-$Me_2C_6H_3$) after 2 days, while 3 days were necessary for **1c**. The lower yields obtained for **1b** and **1c** were probably due to partial decomposition and their high solubility in hexane. However, when these reactions were monitored by ^1H NMR spectroscopy, they proceeded almost quantitatively without C−H activation of the ortho substituents, as previously observed for related alkoxo complexes with this type of R group.[26,27]

The different R groups were also responsible for the differences found in the ^1H and ^{13}C NMR spectra at 20 °C. At this temperature, the ^1H NMR spectrum of **1a** (R = *Sii*Pr$_3$) showed two resonances at δ 0.10 and δ 0.21, with relative intensity 1:2, for two different tantalum-methyl groups, as expected for a nonfluxional molecule with a "pseudo-square-pyramidal" geometry. However the ^1H NMR spectra of complexes **1b** (R = 2,6-$Me_2C_6H_3$) and **1c** (R = 2,6-*i*$Pr_2C_6H_3$) show a broad resonance for three equivalent tantalum-bound methyl groups on the NMR time scale, indicating that most likely they are made equivalent by a Berry pseudorotation.[28,29] For this reason VT-DNMR and NOE experiments were carried out to conclude that the methyl ^1H NMR resonances for **1a** coalesce at 40 °C, corresponding approximately to a barrier rearrangement of $\Delta G^\#$ = 67.2(2) kJ mol^{-1}. Similar behavior was also observed for complexes **1b** and **1c** when they were cooled, showing coalescence of their methyl resonances at −32 °C (**1b**) and −37 °C (**1c**) with $\Delta G^\#$ barriers of 55.3(2) and 50.5(2) kJ mol^{-1}, respectively. The increasing value of the energy barrier from **1c** to **1a** is related to the increasing π donation of the oxygen atom.[30,31]

Synthesis of Cationic Compounds. Compounds **1** reacted with $B(C_6F_5)_3$ in toluene to give the ionic complexes $[TaCp^*Me_2(OR)][MeB(C_6F_5)_3]$ (R = Si*i*Pr$_3$, **2a-B**; 2,6-$Me_2C_6H_3$, **2b-B**; 2,6-*i*$Pr_2C_6H_3$, **2c-B**) as yellowish oils characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy (Scheme 1). Complexes **2-B** were insoluble in toluene but soluble in halogenated solvents and thermally stable for long periods in the absence of moisture. The ^1H and ^{13}C NMR spectra of these complexes showed one resonance for the two equivalent Ta-Me groups clearly shifted low field with respect to those observed for the corresponding parent compounds **1**, and a broad signal corresponding to the boron-bound methyl group was also observed in the ^1H NMR spectra at about δ 0.50. The absence of an ion-pair interaction is consistent with the $\delta_{meta}-\delta_{para}$ differences found in the ^{19}F NMR spectra[32] below 2.8 ppm, as previously reported for similar monocyclopentadienyl tantalum cationic compounds.[24]

Cations **2** were also cleanly obtained by protonolysis of $[TaCp^*Me_3]^+$ with ROH. This process was immediate at 20 °C for **2a** and **2b**, whereas formation of **2c**, with the bulkier 2,6-*i*$Pr_2C_6H_3$ substituent, required 6 h. Nevertheless, the conditions for this protonolysis were milder than those required for the synthesis of the neutral compounds **1** and reaction at the Me−B or C_6F_5−B bonds of the anion were never observed.

In a way analogous to the formation of compounds **2-B**, abstraction of one methyl group by reaction of complexes **1** with the Lewis acid $Al(C_6F_5)_3$ afforded the related ionic derivatives $[TaCp^*Me_2(OR)][MeAl(C_6F_5)_3]$ (R = Si*i*Pr$_3$, **2a-Al**; 2,6-$Me_2C_6H_3$, **2b-Al**; 2,6-*i*$Pr_2C_6H_3$, **2c-Al**) (Scheme 1). Compounds **2-Al** were obtained as yellow waxes insoluble in toluene but soluble in halogenated solvents. The ^1H and ^{13}C NMR spectra of the cations of complexes **2-B** and **2-Al** containing the same R group also showed the same resonances, as expected for the identical cationic moieties $[TaCp^*Me_2(OR)]^+$ (**2**) without an ion-pair interaction. All three compounds **2-Al** contain the same anion $[MeAl(C_6F_5)_3]^-$, which was identified by means of one resonance in the ^1H NMR spectra about −0.50 ppm, for the Me-Al group, and the three resonances in the ^{19}F NMR spectra at about −120.0 (*o*-C_6F_5), −156.0 (*p*-C_6F_5), and −161.0 (*m*-C_6F_5).

It has been reported that the larger covalent radius of the aluminum atom compared with the boron atom justified its increased capacity to abstract two methyl groups from the metal center.[33,34] Both Lewis acids $B(C_6F_5)_3$ and $Al(C_6F_5)_3$ have also been observed to form dinuclear anions of the type $[X\{E(C_6F_5)_3\}_2]^-$.[21,22,35,36] This different behavior prompted us to study reactions of compounds **1** with excess $B(C_6F_5)_3$ and $Al(C_6F_5)_3$.

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Table 1. Polymerization of MMA[a]

run	complex	T (°C)	time (h)	yield (%)	M_n calc[b]	$10^5 M_n$ (g/mol)	M_w/M_n[c]	[rr] (%)[d]	[mr] (%)[d]	[mm] (%)[d]
1	[TaCp*Me$_4$]	40	6	74	9260	1.67	1.58	68	30	2
2	[TaCp*Me$_4$]	60	3	37	4630	0.83	1.65	66	32	2
3	[TaCp*Me$_4$]	60	6	100	12 515	0.85	2.03	67	30	3
4	**1a**	60	6	100	12 515	4.93	2.52	73	25	2
5	**1b**	60	6	68	8510	8.58	1.36	71	27	2

[a] Polymerization conditions: [TaCp*Me$_3$X] (0.08 mmol) and Al(C$_6$F$_5$)$_3$ (0.12 mmol) premixed in toluene (4 mL), then MMA (1 g; [MMA]:[Ta] = 125:1). [b] M_n calc values = conv × [MMA]/[Ta] × 100.81 g mol^{-1} (100.81 = fw MMA). [c] Determined by GPC in THF vs polystyrene standars. [d] Determined by ^{1}H NMR in CDCl$_3$.

When 2 equiv of B(C$_6$F$_5$)$_3$ were used, no further reaction was observed and the unique final products were the ionic compounds with the mononuclear anion **2-B** and the free borane compound. However, when these reactions were carried out using excess Al(C$_6$F$_5$)$_3$, the new complexes [TaCp*Me$_2$(OR)]-[Me{Al(C$_6$F$_5$)$_3$}$_2$] (R = Si*i*Pr$_3$, **2a-Al2**; 2,6-Me$_2$C$_6$H$_3$, **2b-Al2**; 2,6-*i*Pr$_2$C$_6$H$_3$, **2c-Al2**) containing the dinuclear anion were isolated (Scheme 1). Compounds **2-Al2** showed solubility similar to that observed for compounds **2-B** and **2-Al**, although they were far less stable in dichloromethane, probably due to the lower stability of the Al−C bonds. The nonassociative nature of the ion pair gave rise to almost identical ^{1}H and ^{13}C NMR spectra, corresponding with the unmodified nature of the cations [TaCp*Me$_2$(OR)]$^+$ (**2**). The ^{19}F NMR spectra showed three new resonances for the dinuclear anion [(C$_6$F$_5$)$_3$Al−Me−Al(C$_6$F$_5$)$_3$]$^-$, the most striking feature being the low-field shift of the *p*-fluorine resonances from ca. −155 ppm to ca. −150 ppm, which is consistent with the decreasing negative charge of the aluminum center.

In view of these results, we also explored the behavior of the peralkylated compound [TaCp*Me$_4$] with the Lewis acid Al(C$_6$F$_5$)$_3$, taking into account that [TaCp*Me$_4$] had been previously used as precursor of a stable cationic complex when reacted with B(C$_6$F$_5$)$_3$.[24] Abstraction of one methyl group of [TaCp*Me$_4$] with 1 equiv of Al(C$_6$F$_5$)$_3$ afforded the ionic compound [TaCp*Me$_3$][MeAl(C$_6$F$_5$)$_3$] (**3-Al**) as a yellowish oil soluble in halogenated solvents but insoluble in toluene (Scheme 1). The ^{1}H and ^{13}C NMR spectra of **3-Al** showed one resonance for the three equivalent Me-Ta groups clearly shifted low field with respect to that corresponding to the parent compound [TaCp*Me$_4$]. These resonances are essentially the same as observed in the ^{1}H and ^{13}C NMR spectra of cation **3** in [TaCp*Me$_3$][MeB(C$_6$F$_5$)$_3$] (**3-B**) and points to the absence of an ion-pairing interaction, as in the other ionic complexes described in this paper. A broad signal at about δ −0.60 corresponding to the Me-Al group was also observed in the ^{1}H NMR spectra. The ^{19}F NMR spectrum of **3-Al** is analogous to that described for compounds **2-Al**.

An analogous reaction of [TaCp*Me$_4$] with 2 equiv of Al(C$_6$F$_5$)$_3$ in toluene gave a mixture of compound **3-Al** and [TaCp*Me$_3$][Me{Al(C$_6$F$_5$)$_3$}$_2$] (**3-Al2**), characterized by the signals found in the ^{19}F NMR spectrum (Scheme 1). However, the ^{1}H NMR spectrum showed only the set of resonances corresponding to the same cation **3** for both complexes **3-Al** and **3-A2**. We could not obtain **3-Al2** as a pure product when working in toluene, as stirring for longer periods led to partial decomposition even in a glovebox. Furthermore, any attempt to reproduce this reaction in chlorinated solvents afforded a mixture of **3-Al**, **3-Al2**, and other unidentified compounds.

The reactions of the ionic derivative **3-Al** with the alcohols used in this work were also investigated by NMR spectroscopy. For R = Si*i*Pr$_3$, total transformation into **2a-Al** was observed. However, for R = 2,6-Me$_2$C$_6$H$_3$ and 2,6-*i*Pr$_2$C$_6$H$_3$ a mixture of compounds was obtained, with **2b-Al** as the major component for R = 2,6-Me$_2$C$_6$H$_3$, whereas **2c-Al** was the minor product for R = 2,6-*i*Pr$_2$C$_6$H$_3$. Probably, reaction at the tantalum atom was the kinetic product and increasing steric hindrance at the aryl substituents favored the formation of the thermodynamically more stable aluminum alkoxo compounds, although identification of compounds different from complexes **2** was not possible.

MMA Polymerization. The neutral compounds [TaCp*Me$_3$X] (X = OR, Me) were studied as catalysts for MMA polymerization in the presence of the Lewis acids E(C$_6$F$_5$)$_3$ (E = B, Al), taking into account that compounds [TaCp*Me$_3$X] and E(C$_6$F$_5$)$_3$ did not polymerize MMA alone under the conditions employed in this work. For E = B no polymerization was observed, while for E = Al all of the complexes except **1c** were active, although heating was necessary (Table 1). Apparently, the steric hindrance of the 2,6-*i*Pr$_2$C$_6$H$_3$ groups was clearly responsible for the lack of activity of this last compound. We have also checked that excess Al(C$_6$F$_5$)$_3$ was necessary for suitable MMA polymerization, but addition of 2 equiv was not an essential requirement.

Polymerization with [TaCp*Me$_4$] showed an increase in PDI (M_n/M_w) with temperature (run 1 vs 3) and with time (run 2 vs 3), as shown in Table 1. In contrast, the polymer length decreased with increasing temperature (run 1 vs 3), whereas it remained unmodified for longer reaction times (run 2 vs 3). With respect to the alkoxo complexes [TaCp*Me$_3$(OR)] (R = Si*i*Pr$_3$, **1a**; 2,6-Me$_2$C$_6$H$_3$, **1b**), high molecular weight PMMA with broad PDI was produced with **1a** (run 4), while compound **1b** produced the PMMA with the highest molecular weight and narrowest PDI of all experiments (run 5). However, the observed differences between the calculated and the experimental M_n indicated low-efficiency systems. The alkoxo derivatives produced PMMA with higher syndiotacticity than that obtained with [TaCp*Me$_4$]. The PDI values obtained from GPC measurements, supported by the GPC diagrams of the polymers, showed that the active species generated from complex **1b** was the most stable, whereas that generated from **1a** did not remain unchanged, according to the shoulder observed in its GPC diagram. Similar behavior was observed for [TaCp*Me$_4$] at 60 °C compared to 40 °C, demonstrated by the increasing PDI values (runs 1 and 2 vs 3). The presence of two ortho-methyl substitutes in the aryloxo ligand in the precursor **1b** seems to be the reason for the higher stability of the active species.

For a better understanding of the initiation step of the MMA polymerization, the behavior of the ionic complexes [TaCp*Me$_2$X]-[MeE(C$_6$F$_5$)$_3$] (X = OR, Me; E = B, Al) in the presence of 1 equiv or an excess of MMA was monitored by NMR spectroscopy. While no reaction was observed for E = B after heating at 60 °C for several hours, addition of 1 equiv of E = Al gave rise to a mixture of complexes [TaCp*Me$_3$X] (X = OR, Me) and [TaCp*Me$_2$X][MeAl(C$_6$F$_5$)$_3$] (X = OR, **2-Al**; Me, **3-Al**) and the adduct MMA·Al(C$_6$F$_5$)$_3$. These mixtures evolved slowly at ambient temperature to give PMMA and the recovered cation [TaCp*Me$_2$X]$^+$. In the ^{19}F NMR spectra resonances for the

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anion $[MeAl(C_6F_5)_3]^-$ and the adducts $MMA{\cdot}Al(C_6F_5)_3$ and $PMMA{\cdot}Al(C_6F_5)_3$ were observed. Addition of excess MMA (6 equiv) showed the same behavior, with the starting ionic compounds also slowly recovered. When a huge excess of MMA (20 equiv) was added, the appearance of new resonances consistent with the formation of enolaluminato anions was detected in the ^{19}F NMR spectra, as described by Chen et al. for MMA polymerization using $Al(C_6F_5)_3$ as cocatalyst.[10,15] However, these new resonances were clearly due to a minor component, indicating that formation of the active species was not favored. It is noteworthy that this process was also observed for the derivative **1c**, although was clearly much slower, this being the reason for the lack of activity observed experimentally.

These results were in accordance with a bimolecular mechanism where the polymer chain grows on the aluminum center, the polymerization being initiated by methyl transfer from the tantalum atom to the adduct $MMA{\cdot}Al(C_6F_5)_3$. The slowness in this methyl transfer, as was demonstrated in the NMR experiments described above where the resonances belonging to the enolaluminate species were clearly minor, justifies the low efficiency of these polymerization systems.

Conclusions

Protonolysis of a Ta−Me bond in complex $[TaCp^*Me_4]$ with several alcohol compounds has been proved to be a suitable method for the synthesis of new monocyclopentadienyl monoalkoxo complexes $[TaCp^*Me_3(OR)]$ (R = Si*i*Pr$_3$, **1a**; 2,6-$Me_2C_6H_3$, **1b**; 2,6-*i*$Pr_2C_6H_3$, **1c**), although electronic and steric characteristics of the ROH compounds exerted an important influence in the reaction conditions. These alkoxo derivatives are precursors of the cationic compounds $[TaCp^*Me_2(OR)]^+$ on reaction with the Lewis acids $E(C_6F_5)_3$ (E = B, Al). In the particular case of E = Al, addition of an excess afforded a dimetallic counteranion $[Me\{Al(C_6F_5)_3\}_2]^-$, due to the longer covalent radius of the Al atom compared with the B atom. The same behavior was observed for $[TaCp^*Me_4]$ upon reaction with 1 and 2 equiv of $Al(C_6F_5)_3$. The complexes $[TaCp^*Me_3X]$ (X = OR {R = Si*i*Pr$_3$, 2,6-$Me_2C_6H_3$}, Me) polymerized MMA when activated with $Al(C_6F_5)_3$, but not in the presence of $B(C_6F_5)_3$, yielding high molecular weight PMMA for the alkoxo derivatives, although the efficiency of these systems was low.

Experimental Section

General Considerations. All manipulations were carried out under an argon atmosphere, and solvents were distilled from appropriate drying agents. NMR spectra were recorded at 400.13 (^1H), 376.70 (^{19}F), and 100.60 (^{13}C) MHz on a Bruker AV400. Chemical shifts (δ) are given in ppm relative to internal TMS (^1H and ^{13}C) or external $CFCl_3$ (^{19}F). Elemental analyses were performed on a Perkin-Elmer 240C. Compounds $[TaCp^*Me_4]$,[37] $[TaCp^*Me_3][MeB(C_6F_5)_3]$ (**3-B**),[24] $B(C_6F_5)_3$,[38] and 0.5(toluene)$\cdot Al(C_6F_5)_3$[21] were prepared by literature methods. ROH was purchased from Aldrich, degassed, and stored under Ar with molecular sieves (R = Si*i*Pr$_3$, 2,6-*i*$Pr_2C_6H_3$) or sublimed under vacuum (R = 2,6-$Me_2C_6H_3$).

[TaCp*Me$_3$(OSi*i*Pr$_3$)] (1a). A solution of $[TaCp^*Me_4]$ (0.300 g, 0.80 mmol) and *i*Pr_3SiOH (0.160 g, 0.83 mmol) in toluene (10 mL) was stirred at room temperature for 16 h. The volatiles were then removed under vacuum, and hexane was added (15 mL). The solution was filtered, and the volume was concentrated to ca. 4 mL and cooled to −40 °C, yielding **1a** as yellow crystals (0.33 g, 78%). Data for **1a**: ^1H NMR ($CDCl_3$) 0.10 (s, 3 H, *Me*-Ta), 0.21 (s, 6 H, *Me*-Ta), 1.06 (m, 21 H, *Me$_2$*CH and Me$_2$C*H*), 1.93 (s, 15 H, C$_5$*Me$_5$*); ^{13}C NMR ($CDCl_3$) 11.1 (C$_5$*Me$_5$*), 12.9 (Me$_2$*C*H), 18.0 (*Me$_2$*CH), 50.0 (*Me*-Ta), 51.5 (*Me*-Ta), 115.9 (*C$_5$*Me$_5$). Anal. Calc for $C_{22}H_{45}OSiTa$ (534.63): C, 49.42; H, 8.48. Found: C, 49.10; H, 8.33.

[TaCp*Me$_3$(OR)] (R = 2,6-Me$_2$C$_6$H$_3$ 1b). A solution of $[TaCp^*Me_4]$ (0.300 g, 0.80 mmol) and ROH (R = 2,6-$Me_2C_6H_3$) (0.087 g, 0.72 mmol) in toluene (5 mL) was heated at 100 °C for 48 h. The volatiles were then removed under vacuum, and hexane was added (20 mL). The solution was filtered, and the volume was concentrated to ca. 10 mL and cooled to −40 °C, yielding **1b** as yellow crystals (0.170 g, 50%). A second crop was obtained from concentrating the previous solution to ca. 5 mL and cooling to −40 °C (0.052 g, 15%). Data for **1b**: ^1H NMR ($CDCl_3$) 0.26 (s, 9 H, *Me*-Ta), 1.99 (s, 15 H, C$_5$*Me$_5$*), 2.32 (s, 6 H, *Me$_2$*C$_6$H$_3$), 6.75 (m, 1 H, Me$_2$C$_6$*H$_3$*), 6.97 (m, 2 H, Me$_2$C$_6$*H$_3$*); ^{13}C NMR ($CDCl_3$): 11.4 (C$_5$*Me$_5$*), 19.8 (*Me$_2$*C$_6$H$_3$), 52.7 (*Me*-Ta), 115.6 (*C$_5$*Me$_5$), 121.4, 126.8, 128.6, and 161.0 (Me$_2$*C$_6$*H$_3$). Anal. Calc for $C_{21}H_{33}OTa$ (482.43): C, 52.28; H, 6.89. Found: C, 52.10; H, 6.85.

[TaCp*Me$_3$(OR)] (R = 2,6-*i*Pr$_2$C$_6$H$_3$ 1c). The same procedure as above but heating for 3 days afforded **1c** as yellow crystals (0.300 g, 70%). Data for **1c**: ^1H NMR ($CDCl_3$) 0.22 (s, 9 H, *Me*-Ta), 1.19 (d, 12 H, ^3J(H−H) = 6.7 Hz, *Me$_2$*CH), 1.97 (s, 15 H, C$_5$*Me$_5$*), 3.37 (sept., 2 H, ^3J(H−H) = 6.7 Hz, Me$_2$C*H*), 6.94 (m, 1 H, Me$_2$C$_6$*H$_3$*), 7.07 (m, 2 H, Me$_2$C$_6$*H$_3$*); ^{13}C NMR ($CDCl_3$) 11.1 (C$_5$*Me$_5$*), 24.4 (*Me$_2$*CH), 26.3 (Me$_2$*C*H), 51.7 (*Me*-Ta), 116.4 (*C$_5$*Me$_5$), 122.1, 123.6, 137.1, and 157.6 (*C$_6$*H$_3$). Anal. Calc for $C_{25}H_{41}OTa$ (538.54): C, 55.76; H, 7.67. Found: C, 55.46; H, 7.29.

[TaCp*Me$_2$(OR)][MeB(C$_6$F$_5$)$_3$] (R = Si*i*Pr$_3$ 2a-B, 2,6-Me$_2$C$_6$H$_3$ 2b-B, 2,6-*i*Pr$_2$C$_6$H$_3$ 2c-B). $[TaCp^*Me_3(OR)]$ (**1a** 0.100 g, 0.19 mmol; **1b** 0.100 g, 0.21 mmol; **1c** 0.100 g, 0.19 mmol) and $B(C_6F_5)_3$ (1.2 equiv) were stirred in toluene (5 mL) for 5 min. The solution was then filtered, leaving an oil that was washed first with toluene (3 mL) and then with hexane (2 × 3 mL), obtaining **2-B** as brownish oils (**2a-B** 0.17 g, 86%; **2b-B** 0.16 g, 79%; **2c-B** 0.17 g, 85%).

Data for **2a-B**: ^1H NMR (CD_2Cl_2) 0.73 (bs, 3 H, *Me*-B), 1.10 (s, 6 H, *Me*-Ta), 1.24 (m, 21 H, *Me$_2$*CH and Me$_2$C*H*), 2.27 (s, 15 H, C$_5$*Me$_5$*); ^{13}C NMR (CD_2Cl_2) 11.7 (C$_5$*Me$_5$*), 13.6 (Me$_2$*C*H), 17.5 (*Me$_2$*CH), 68.7 (*Me*-Ta), 126.0 (*C$_5$*Me$_5$), 135.4 (m, *C$_6$*F$_5$), 138.9 (m, *C$_6$*F$_5$), 148.3 (m, *C$_6$*F$_5$); ^{19}F NMR (CD_2Cl_2) −131.3 (*o*-C$_6$F$_5$), −163.7 (*p*-C$_6$F$_5$), −166.2 (*m*-C$_6$F$_5$). Anal. Calc for $C_{40}H_{45}BF_{15}OSiTa$ (1046.61): C, 45.90; H, 4.33. Found: C, 46.01; H, 4.48.

Data for **2b-B**: ^1H NMR (CD_2Cl_2) 0.46 (bs, 3 H, *Me*-B), 1.35 (s, 6 H, *Me*-Ta), 2.19 (s, 6 H, *Me$_2$*C$_6$H$_3$), 2.26 (s, 15 H, C$_5$*Me$_5$*), 7.23 (m, 3 H, Me$_2$C$_6$*H$_3$*); ^{13}C NMR (CD_2Cl_2) 11.5 (C$_5$*Me$_5$*), 16.9 (*Me$_2$*C$_6$H$_3$), 70.9 (*Me*-Ta), 125.4, 126.9, 128.4, 129.2 and 161.0 (*C$_5$*Me$_5$ and Me$_2$*C$_6$*H$_3$), 135.4 (m, *C$_6$*F$_5$), 138.7 (m, *C$_6$*F$_5$), 148.2 (m, *C$_6$*F$_5$); ^{19}F NMR (CD_2Cl_2) −130.0 (*o*-C$_6$F$_5$), −162.1 (*p*-C$_6$F$_5$), −164.7 (*m*-C$_6$F$_5$). Anal. Calc for $C_{39}H_{33}BF_{15}OTa$ (994.41): C, 47.10; H, 3.34. Found: C, 47.20; H, 3.18.

Data for **2c-B**: ^1H NMR (CD_2Cl_2) 0.46 (bs, 3 H, *Me*-B), 1.27 (d, 12 H, ^3J(H−H) = 6.8 Hz, *Me$_2$*CH), 1.31 (s, 6 H, *Me*-Ta), 2.23 (s, 15 H, C$_5$*Me$_5$*), 2.54 (sept., 2 H, ^3J(H−H) = 6.8 Hz, Me$_2$C*H*), 7.25 (m, 3 H, Me$_2$C$_6$*H$_3$*); ^{13}C NMR (CD_2Cl_2) 11.4 (C$_5$*Me$_5$*), 23.3 (*Me$_2$*CH), 28.3 (Me$_2$*C*H), 71.0 (*Me*-Ta), 124.5, 126.0, 127.5, 128.4, and 153.7 (*C$_5$*Me$_5$ and *C$_6$*H$_3$), 136.4 (m, *C$_6$*F$_5$), 137.6 (m, *C$_6$*F$_5$), 147. 5 (m, *C$_6$*F$_5$); ^{19}F NMR (CD_2Cl_2) −131.6 (*o*-C$_6$F$_5$), −163.8 (*p*-C$_6$F$_5$), −166.3 (*m*-C$_6$F$_5$). Anal. Calc for $C_{43}H_{41}BF_{15}OTa$ (1050.52): C, 49.16; H, 3.93. Found: C, 48.99 H, 3.73.

[TaCp*Me$_2$(OR)][MeAl(C$_6$F$_5$)$_3$] (R = Si*i*Pr$_3$, 2a-Al; 2,6-Me$_2$C$_6$H$_3$, 2b-Al; 2,6-*i*Pr$_2$C$_6$H$_3$, 2c-Al). $[TaCp^*Me_3(OR)]$ (**1a** 0.100 g, 0.19 mmol; **1b** 0.100 g, 0.21 mmol; **1c** 0.100 g, 0.19 mmol) and $Al(C_6F_5)_3$ (0.9 equiv) were stirred in toluene (5 mL) for 5 min. The solution was then filtered, leaving an oil that was washed first with toluene (3 mL) and then with hexane (2 × 3 mL), obtaining

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(38) Lancaster, S. In www.syntheticpages.org, 2003, p 215.

2-Al as brownish oils (**2a-Al** 0.15 g, 78%; **2b-Al** 0.16 g, 77%; **2c-Al** 0.16 g, 80%).

Data for **2a-Al**: ^{1}H NMR (CD_2Cl_2) −0.30 (bs, 3 H, *Me*-Al), 1.10 (s, 6 H, *Me*-Ta), 1.24 (m, 21 H, Me_2CH and Me_2CH), 2.28 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_2Cl_2) 11.5 (C_5Me_5), 13.6 (Me_2CH), 17.5 (Me_2CH), 68.6 (*Me*-Ta), 125.9 (C_5Me_5), 136.5 (m, C_6F_5), 140.5 (m, C_6F_5), 149.9 (m, C_6F_5), *Me*-Al was not observed; ^{19}F NMR (CD_2Cl_2) −119.8 (*o*-C_6F_5), −155.6 (*p*-C_6F_5), −161.7 (*m*-C_6F_5). Anal. Calc for $C_{40}H_{45}AlF_{15}OSiTa$ (1062.78): C, 45.21; H, 4.27. Found: C, 45.00; H, 4.18.

Data for **2b-Al**: ^{1}H NMR (CD_2Cl_2) −0.27 (bs, 3 H, *Me*-Al), 1.35 (s, 6 H, *Me*-Ta), 2.19 (s, 6 H, $Me_2C_6H_3$), 2.26 (s, 15 H, C_5Me_5), 7.25 (m, 3 H, $Me_2C_6H_3$); ^{13}C NMR (CD_2Cl_2) 11.1 (C_5Me_5), 16.6 ($Me_2C_6H_3$), 70.5 (*Me*-Ta), 125.6, 126.4, 128.0, 129.2 and 156.2 (C_5Me_5 and $Me_2C_6H_3$), 135.4 (m, C_6F_5), 138.6 (m, C_6F_5), 149.5 (m, C_6F_5), *Me*-Al was not observed; ^{19}F NMR (CD_2Cl_2) −120.0 (*o*-C_6F_5), −155.6 (*p*-C_6F_5), −161.8 (*m*-C_6F_5). Anal. Calc for $C_{39}H_{33}AlF_{15}OTa$ (1010.58): C, 46.35; H, 3.29. Found: C, 45.90; H, 3.15.

Data for **2c-Al**: ^{1}H NMR (CD_2Cl_2) −0.40 (bs, 3 H, *Me*-Al), 1.27 (d, 12 H, ^3J(H−H) = 6.7 Hz, Me_2CH), 1.35 (s, 6 H, *Me*-Ta), 2.24 (s, 15 H, C_5Me_5), 2.58 (sept., 2 H, ^3J(H−H) = 6.7 Hz, Me_2CH), 6.94 (m, 1 H, $Me_2C_6H_3$), 7.22 (m, 3 H, $Me_2C_6H_3$); ^{13}C NMR (CD_2Cl_2) 11.1 (C_5Me_5), 24.0 (Me_2CH), 28.7 (Me_2CH), 71.7 (*Me*-Ta), 124.3, 126.1, 128.5, 139.3, and 154.9 (C_5Me_5 and C_6H_3), 135.8 (m, C_6F_5), 139.1 (m, C_6F_5), 149.5 (m, C_6F_5), *Me*-Al was not observed; ^{19}F NMR (CD_2Cl_2) −119.2 (*o*-C_6F_5), −156.6 (*p*-C_6F_5), −161.6 (*m*-C_6F_5). Anal. Calc for $C_{43}H_{41}AlF_{15}OTa$ (1066.69): C, 48.42; H, 3.87. Found: C, 48.57; H, 3.77.

[TaCp*Me$_2$(OR)][Me{Al(C$_6$F$_5$)$_3$}$_2$] (R = Si*i*Pr$_3$, 2a-Al2; 2,6-Me$_2$C$_6$H$_3$, 2b-Al2; 2,6-*i*Pr$_2$C$_6$H$_3$, 2c-Al2). A solution of [TaCp*Me$_3$(OR)] (**1a** 0.050 g, 0.093 mmol; **1b** 0.045 g, 0.093 mmol; **1c** 0.050 g, 0.093 mmol) and 0.5(toluene)·Al(C_6F_5)$_3$ (0.135 g, 0.23 mmol) in CH_2Cl_2 (3 mL) was stirred for 30 min. The volatiles were then removed, and the remaining oil was washed first with toluene (5 mL) and then with hexane (5 mL) to give **2-Al2** as brownish oils (**2a-Al2** 0.10 g, 70%; **2b-Al2** 0.11 g, 72%; **2c-Al2** 0.11 g,72%). These compounds were characterized only by NMR spectroscopy due to their high sensitivity to air and moisture.

Data for **2a-Al2**: ^{1}H NMR (CD_2Cl_2) 1.11 (s, 6 H, *Me*-Ta), 1.18 (m, 21 H, Me_2CH and Me_2CH), 2.30 (s, 15 H, C_5Me_5), *Me*-Al was not observed; ^{13}C NMR (CD_2Cl_2) 11.7 (C_5Me_5), 13.6 (Me_2CH), 17.1 (Me_2CH), 68.9 (*Me*-Ta), 126.2 (C_5Me_5), 135.6 (m, C_6F_5), 138.8 (m, C_6F_5), 148.1 (m, C_6F_5), *Me*-Al was not observed; ^{19}F NMR (CD_2Cl_2) −120.8 (*o*-C_6F_5), −153.4 (*p*-C_6F_5), −161.9 (*m*-C_6F_5).

Data for **2b-Al2**: ^{1}H NMR (CD_2Cl_2) 0.46 (bs, 3 H, *Me*-B), 1.35 (s, 6 H, *Me*-Ta), 2.19 (s, 6 H, $Me_2C_6H_3$), 2.26 (s, 15 H, C_5Me_5), 7.20 (m, 3 H, $Me_2C_6H_3$), *Me*-Al was not observed; ^{13}C NMR (CD_2Cl_2) 11.2 (C_5Me_5), 16.6 ($Me_2C_6H_3$), 70.6 (*Me*-Ta), 125.4, 125.6, 126.5, 128.8, 129.2 and 156.2 (C_5Me_5 and $Me_2C_6H_3$), 135.8 (m, C_6F_5), 141.5 (m, C_6F_5), 149.5 (m, C_6F_5), *Me*-Al was not observed; ^{19}F NMR (CD_2Cl_2) −120.5 (*o*-C_6F_5), −152.8 (*p*-C_6F_5), −161.5 (*m*-C_6F_5).

Data for **2c-Al2**: ^{1}H NMR (CD_2Cl_2) 1.27 (d, 12 H, ^3J(H−H) = 6.8 Hz, Me_2CH), 1.33 (s, 6 H, *Me*-Ta), 2.24 (s, 15 H, C_5Me_5), 2.55 (sept., 2 H, ^3J(H−H) = 6.8 Hz, Me_2CH), 7.20 (m, 3 H, $Me_2C_6H_3$), *Me*-Al was not observed; ^{13}C NMR (CD_2Cl_2) 11.6 (C_5Me_5), 23.5 (Me_2CH), 28.4 (Me_2CH), 71.2 (*Me*-Ta), 124.6, 126.1, 128.0, 129.3, and 153.7 (C_5Me_5 and C_6H_3), 136.7 (m, C_6F_5), 141.7 (m, C_6F_5), 150.3 (m, C_6F_5), *Me*-Al was not observed; ^{19}F NMR (CD_2Cl_2) −120.5 (*o*-C_6F_5), −153.1 (*p*-C_6F_5), −161.6 (*m*-C_6F_5).

[TaCp*Me$_3$][MeAl(C$_6$F$_5$)$_3$] (3-Al). [TaCp*Me$_4$] (0.100 g, 0.26 mmol) and 0.5(toluene)·Al(C_6F_5)$_3$ (0.135 g, 0.23 mmol) were stirred in toluene (5 mL) for 15 min. The solution was then filtered off, leaving an oil that was washed with hexane (2 × 5 mL), obtaining **3-Al** as a brownish oil (0.13 g, 70%). Data for **3-Al**: ^{1}H NMR (CD_2Cl_2) −0.44 (bs, 3 H, *Me*-Al), 1.34 (s, 9 H, *Me*-Ta), 2.26 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_2Cl_2) 12.4 (C_5Me_5), 86.8 (*Me*-Ta), 125.2 (C_5Me_5), 136.0 (m, C_6F_5), 138.2 (m, C_6F_5), 148.7 (m, C_6F_5), *Me*-Al was not observed; ^{19}F NMR (CD_2Cl_2) −119.0 (*o*-C_6F_5), −156.5 (*p*-C_6F_5), −161.5 (*m*-C_6F_5). Anal. Calc for $C_{32}H_{27}AlF_{15}Ta$ (904.46): C, 42.49; H, 3.01. Found: C, 43.10; H, 3.14.

[TaCp*Me$_3$][Me{Al(C$_6$F$_5$)$_3$}$_2$] (3-Al2). [TaCp*Me$_4$] (0.020 g, 0.05 mmol) and 0.5(toluene)·Al(C_6F_5)$_3$ (0.068 g, 0.12 mmol) were stirred in toluene (2 mL) for 2 days. The solution was filtered, leaving an oil that was washed with toluene (3 mL) and hexane (2 × 3 mL), to give a mixture of **3-Al** and **3-Al2** in ca. 1:0.5 molar ratio. Data for **3-Al2**: ^{1}H NMR (CD_2Cl_2) 1.34 (s, 9 H, *Me*-Ta), 2.26 (s, 15 H, C_5Me_5), *Me*-Al was not observed; ^{19}F NMR (CD_2Cl_2) −120.0 (*o*-C_6F_5), −153.0 (*p*-C_6F_5), −161.7 (*m*-C_6F_5).

Polymerization of MMA. [TaCp*Me$_3$X] (0.08 mmol) and Al(C_6F_5)$_3$ (0.12 mmol) were premixed in 4 mL of toluene in a Teflon-valved ampule, and MMA (1 g; [MMA]:[Ta] = 125:1) was added. The ampule was heated with stirring at the corresponding temperature. The polymerization was terminated by adding MeOH/HCl. The isolated polymer was washed first with MeOH/HCl and then with MeOH/water and dried overnight in vacuo at 60 °C. A ^{1}H NMR ($CDCl_3$) spectrum of the polymer was obtained to determine its tacticity. Melting temperatures of polymers were measured by differential scanning calorimetry (DSC, Perkin-Elmer DSC6). Gel permeation chromatography (GPC) analyses of polymer samples were carried out in THF at 25 °C (Waters GPCV-2000).

Acknowledgment. We gratefully acknowledge Ministerio de Educación y Ciencia (project MAT2004-02614) and DGUI-Comunidad de Madrid (programme S-0505/PPQ-0328, COMAL-CM) (Spain) for financial support. We also thank Prof. Dra. Pilar Tarazona and Gema Marcelo of Departamento de Química-Física (Universidad de Alcalá) for their help on GPC measurements and interpretation.

Supporting Information Available: VT-NMR experiments of compound **1c**, NMR experiments of reaction of **2-Al** with MMA, and GPC diagrams of PMMA. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070166+