Synthesis of neutral and cationic monocyclopentadienyl alkyl niobium and tantalum complexes

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ABSTRACT

Compound [NbCp′Me$_4$] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$, **1**) reacted with several ROH compounds (R = tBu, SiiPr$_3$, 2,6-Me$_2$C$_6$H$_3$) to give the derivatives [NbCp′Me$_3$(OR)] (R = tBu **2a**, SiiPr$_3$ **2b**, 2,6-Me$_2$C$_6$H$_3$ **2c**). The diaryloxo tantalum compound [TaCp*Me$_2$(OR)$_2$] (Cp* = η^5-C$_5$Me$_5$, R = 2,6-Me$_2$C$_6$H$_3$ **3**) was obtained by reaction of [TaCp*Cl$_2$Me$_2$] with 2 equiv of LiOR (R = 2,6-Me$_2$C$_6$H$_3$). Abstraction of one methyl group from these neutral compounds **1**–**3** with the Lewis acids E(C$_6$F$_5$)$_3$ (E = B, Al) gave the ionic derivatives [NbCp′Me$_2$X][MeE(C$_6$F$_5$)$_3$] (X = Me **4**-E. X = OR; R = SiiPr$_3$ **5b**-E, 2,6-Me$_2$C$_6$H$_3$ **5c**-E. E = B, Al) and [TaCp*Me(OR)$_2$][MeE(C$_6$F$_5$)$_3$] (R = 2,6-Me$_2$C$_6$H$_3$ **6**-E; E = B, Al). Polymerization of MMA with the aryloxoniobium compound **2c** and Al(C$_6$F$_5$)$_3$ gave syndiotactic PMMA in a low yield, whereas the tetramethylniobium compound **1** and the diaryloxotantalum derivative **3** were inactive.

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1. Introduction

It is well known that early transition metal alkyl complexes promoted coupling of unsaturated organic substrates, making this process a relevant strategy for organic synthesis and catalytic polymerization [1–4]. In particular, niobium and tantalum alkyl complexes have been applied in C–C coupling reactions via migratory insertion of coordinated unsaturated molecules into the metal alkyl bond [5–16]. In addition, alkyne niobium and tantalum (III) compounds are efficient catalysts for the oligomerization and polymerization of alkynes [17,18] and the formation of alkylidene and alkenyl intermediates through this pathway is commonly accepted [19,20]. However, the number of alkyl mono(cyclopentadienyl) derivatives used for this type of processes is small in part due to their instability [7,13,21–30].

The polymerization of functional alkenes such as acrylates, acrylamides and methacrylates catalyzed by lanthanocenes or group 4 complexes has attracted great attention due to the high activity shown by these systems [31–38]. Applications of group 5 alkyl complexes to this type of polymerization have been less

studied [39–41]. For example, the system [Cp$_2$TaMe$_3$]/2Al(C$_6$F$_5$)$_3$ is highly active for MMA polymerization, although it is completely inactive in other reaction conditions such as catalyst/cocatalyst ratio or different cocatalysts [40].

Recently, we showed that protonolysis of a Ta–Me bond in complex [TaCp*Me$_4$] with several alcohol and silanol compounds was a suitable method for the synthesis of new monocyclopentadienyl complexes [TaCp*Me$_3$(OR)] (R = SiiPr$_3$, 2,6-Me$_2$C$_6$H$_3$, 2,6-iPr$_2$C$_6$H$_3$) [42]. We also reported their reactions with the Lewis acids E(C$_6$F$_5$)$_3$ (E = B, Al) and studies on polymerization of MMA with the systems [TaCp*Me$_3$X]/E(C$_6$F$_5$)$_3$, observing that the polymerization was dependent on the X group (X = Me, OR) and E (E = B, Al). The results showed that polymerization proceeded only when Al(C$_6$F$_5$)$_3$ was the cocatalyst, the best X group was the aryloxo ligand with the 2,6-Me$_2$C$_6$H$_3$ moiety.

As an extension of these studies, and also analogous with the non-cyclopentadienyl group 5 complexes [41], and with the aim of correlating the metal properties to the catalytic behaviour, we have explored the behaviour of new monocyclopentadienyl alkyl niobium complexes [NbCp′Me$_3$(OR)] and a new tantalum dialkyl-diaryloxo compound toward the Lewis acids E(C$_6$F$_5$)$_3$ (E = B, Al), and also their ability as MMA polymerization catalyst. The unexpected results demonstrate that, in spite of their higher Lewis acidity, the niobium complexes are less active for polymerization than the corresponding tantalum derivatives.

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2. Results and discussion

2.1. Synthesis of neutral compounds

The synthesis of the permethylated compound [NbCp′Me$_4$] (**1**) (Cp′ = η^5-C$_5$H$_4$SiMe$_3$) was achieved by reacting the chloro compound [NbCp′Cl$_4$] with 4 equiv of MgClMe, following previously described procedures for the related pentamethylcyclopentadienyl compound [25]. Compound **1** was obtained in good yield as yellow-brown oil, although it is light sensitive and also decomposed slowly at ambient temperature, it was however stable at low temperature for weeks.

Next, we tried the protonolysis reactions of **1** with different alcohols and silanols ROH (R = tBu, SiiPr$_3$, 2,6-Me$_2$C$_6$H$_3$) to obtain the corresponding monosubstituted compounds [NbCp′Me$_3$(OR)] (R = tBu **2a**, SiiPr$_3$ **2b**, 2,6-Me$_2$C$_6$H$_3$ **2c**). The reaction conditions were dependent on the alcohol R group. With the most acidic silanol (iPr$_3$SiOH), the reaction proceeded easily at room temperature, whereas with the bulkier alcohols ROH (R = tBu, 2,6-Me$_2$C$_6$H$_3$), the substitution was slower and required heating to complete the process. In all cases, the monosubstituted derivatives [NbCp′Me$_3$(OR)] (R = tBu **2a**, iPr$_3$Si **2b**, 2,6-Me$_2$C$_6$H$_3$ **2c**) were obtained with moderate yields as brownish oils that were also moisture and also light sensitive. However, these compounds were thermally more stable than the starting compound **1**.

The NMR behaviour of these compounds varies depending on the R groups of the OR substituent. At 25 °C, the ^{1}H NMR spectrum of **2a** (R = tBu) and **2b** (R = iPr$_3$Si) showed two resonances with relative intensities of 1:2 for two different Me−Nb groups, as expected for a non-fluxional molecule. However, the ^{1}H NMR spectrum of complex **2c** (R = 2,6-Me$_2$C$_6$H$_3$) showed a broad resonance corresponding to three equivalent methyl groups attached to niobium, indicating that they had become equivalent in the NMR time scale by a fluxional process, most likely a Berry pseudorotation [43−46], more favourable for the derivative with the less donating siloxo ligand [42,47−49].

To study the influence of a second OR ligand in the coordination sphere of the metal we tried to synthesize compounds of the type [MCp^{R}Me$_2$(OR)$_2$] (M = Nb, Ta). We choose as R group the phenoxo 2,6-Me$_2$C$_6$H$_3$, which in our previous work seemed to be the best ligand to stabilize compounds of this type as well as the hypothetical cationic derivatives that will be studied below. Heating [MCp^{R}Me$_4$] (M = Nb, Cp^R = Cp′; M = Ta, Cp^R = Cp*) with 2 equiv of the corresponding alcohol resulted in the decomposition of the starting compounds or the respective monoaryloxo derivative formed in this procedure. Consequently, we tried an alternative synthetic route consisting of the metathesis reaction of [MCp^{R}Cl$_2$Me$_2$] with LiOAr (Ar = 2,6-Me$_2$C$_6$H$_3$), with this methodology only proving successful for the synthesis of the tantalum compound [TaCp*Me$_2$(OAr)$_2$] (Ar = 2,6-Me$_2$C$_6$H$_3$ **3**), which was obtained as a white solid in good yield. The ^{1}H and ^{13}C NMR spectra of complex **3** showed one singlet for both Ta−Me groups and also one singlet for both methyl groups of Ar moiety. With these data, two possible dispositions of the Me and OAr ligands about the Ta atom can be proposed, cis and trans. However, the size of the OAr ligand could favor a trans disposition (Scheme 1).

2.2. Synthesis of cationic compounds

Mixing [NbCp′Me$_4$] (**1**) with 1 equiv of B(C$_6$F$_5$)$_3$ in toluene at ambient temperature formed an oily precipitate, which was washed with hexane and dissolved in BrC$_6$D$_5$, allowing us to identify the ionic compound [NbCp′Me$_3$][MeB(C$_6$F$_5$)$_3$] (**4**). The ^{1}H NMR spectrum showed a broad singlet at δ 1.05 for the MeB group and three resonances were observed in the ^{19}F NMR spectrum
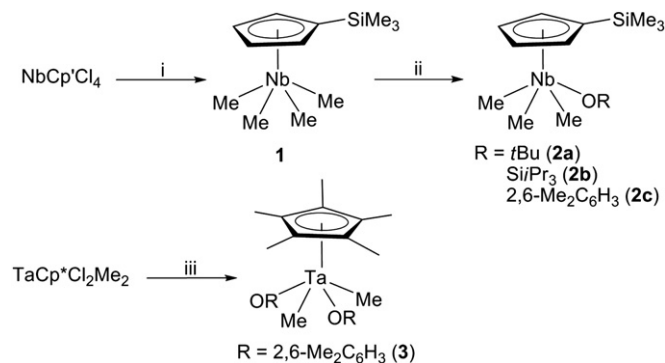

Scheme 1. Synthesis of neutral compounds. i) 4ClMgMe, −78 °C. ii) ROH; r.t., 16 h (R = tBu, SiiPr$_3$); or 60 °C, 24 h (R = 2,6-Me$_2$C$_6$H$_3$). iii) 2LiOR, −78 °C (R = 2,6-Me$_2$C$_6$H$_3$).

corresponding to the free [MeB(C$_6$F$_5$)$_3$]$^-$ anion (Δδ$_{(m,p-F)}$ < 3 ppm) [50]. A similar reaction with Al(C$_6$F$_5$)$_3$ caused **1** to decompose.

In an analogous way to the formation of compound **4**, abstraction of one methyl group of the derivatives **2** with the Lewis acids Al(C$_6$F$_5$)$_3$ or B(C$_6$F$_5$)$_3$ afforded the related ionic derivatives [NbCp′Me$_2$(OR)][MeE(C$_6$F$_5$)$_3$] (R = iPr$_3$Si **5b**-E, 2,6-Me$_2$C$_6$H$_3$ **5c**-E. E = B, Al) (Scheme 2). These ionic compounds were obtained as dark oils insoluble in toluene but soluble in halogenated solvents. However, in the particular case of **2a** only decomposition was observed. It has been reported that the tBu group can be activated, releasing isobutene, although we were not able to detect any byproduct [51,52]. The ^{1}H and ^{13}C NMR spectra of the cationic fragments of complexes containing the same R group, **5b**-B/**5b**-Al and **5c**-B/**5c**-Al showed almost identical ^{1}H and ^{13}C NMR spectra, as expected for identical cationic moieties [NbCp′Me$_2$(OR)]$^+$ without an ion pair interaction. The ^{19}F NMR spectrum of **5B** confirmed this behaviour, with Δδ$_{(m,p-F)}$ < 3 [53]. All of these ionic complexes **4** and **5** decomposed within several hours in BrC$_6$D$_5$ solutions and much faster in CD$_2$Cl$_2$, in contrast to the stability observed for related tantalum derivatives [16,42].

The diaryloxotantalum compound **3** also reacted with 1 equiv of B(C$_6$F$_5$)$_3$ or Al(C$_6$F$_5$)$_3$ in toluene to give the ionic derivatives [TaCp*Me(OR)$_2$][MeE(C$_6$F$_5$)$_3$] (R = 2,6-Me$_2$C$_6$H$_3$; E = B, **6**-B; E = Al, **6**-Al) as brownish oils characterized by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy (Scheme 2). Complexes **6**-B and **6**-Al were insoluble in
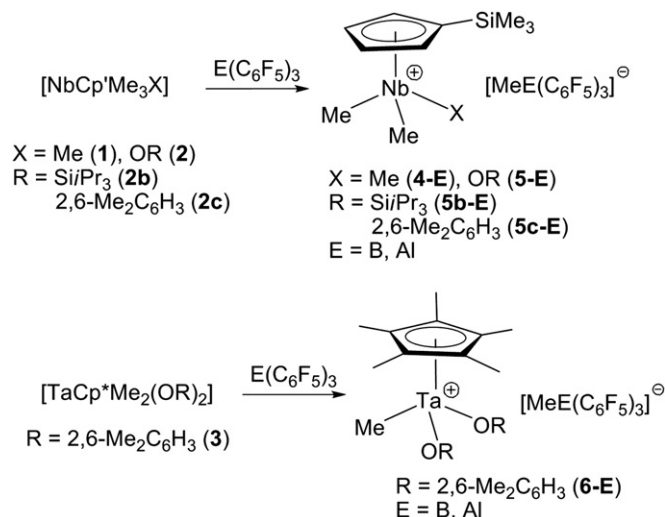
Scheme 2. Synthesis of cationic compounds.

toluene but soluble in halogenated solvents and thermally stable for long periods in the absence of moisture. The ^{1}H and ^{13}C NMR spectra of these complexes showed one resonance for the Ta–Me group clearly shifted to higher frequency with respect to those observed for the corresponding parent compounds **3** and a broad signal corresponding to the methyl Me–B group was also observed in the ^{1}H NMR spectra of **6**-B at about δ 0.50. When Al(C$_6$F$_5$)$_3$ was used the resonance for the abstracted methyl group was not observed in the ^{1}H NMR spectrum. The absence of an ion pair interaction is consistent with the $\Delta\delta_{(m,p\text{-}F)} = 2.5$ found in the ^{19}F NMR spectra [53].

In all these compounds, the Lewis acid E(C$_6$F$_5$)$_3$ (E = B, Al) abstracted the Me group, also in the presence of an oxygen atom bound to the niobium atom, in contrast with the behaviour observed in oxametallacyclic niobium compounds [54].

2.3. MMA polymerization

Neutral monoalkoxo compounds [NbCp′Me$_3$X] (X = Me **1**, X = OR; R = tBu **2a**, SiiPr$_3$ **2b**, 2,6-Me$_2$C$_6$H$_3$ **2c**) were studied as catalysts for MMA polymerization in the presence of the Lewis acids E(C$_6$F$_5$)$_3$ (E = B, Al). Only compound **2c** showed a certain degree of activity ($T = 40$ °C, 16 h, yield 20%) when E = Al while for E = B no polymerization was observed. The polymer obtained was high molecular weight PMMA of narrow polydispersity, predominantly syndiotactic ([rr] 57.9%, [mr] 36.4%, [mm] 5.7%; Mn = 6.10 × 10^5; Mw/Mn = 1.25), as indicated by ^{1}H NMR. The niobium complexes were clearly less effective catalysts than the related tantalum compounds [TaCp*Me$_3$X] (X = Me, OR). The bulkiness of the O(2,6-Me$_2$C$_6$H$_3$) aryloxo ligand of compound **2c** might be the reason for the higher stability of the active species, favoring the polymerization process [42]. In contrast to the related tantalum compound [TaCp*Me$_3$X] (X = Me, OR), increasing temperature did not improve polymerization results with any of these compounds. Also, neither addition of 2 equiv of Al(C$_6$F$_5$)$_3$ led to better results.

On the other hand, the system [TaCp*Me$_2$(OAr)$_2$]/Al(C$_6$F$_5$)$_3$ was inactive for MMA polymerization. This result can be interpreted in terms of the steric hindrance imposed by the presence of two aryloxo groups that avoid the proximity of cation and anion necessary for the initiation step, as was also observed for [TaCp*-Me$_3$(OAr)] (Ar = 2,6-iPr$_2$C$_6$H$_3$) [42].

3. Conclusions

Protonolysis of a Nb–Me bond in complex [NbCp′Me$_4$] has been proved to be a suitable method for the synthesis of new monocyclopentadienyl complexes of the type [NbCp′Me$_3$(OR)], as previously shown for analogous tantalum derivatives, whereas the synthesis of monocyclopentadienyl dialkoxo compounds was only achieved for the tantalum compound [TaCp*Me$_2$(OR)$_2$] by reaction of [TaCp*Cl$_2$Me$_2$] with 2 equiv of LiOR (R = 2,6-Me$_2$C$_6$H$_3$). The electronic and steric characteristics of the ROH compounds have been shown to exert an important influence on the reaction conditions.

These new niobium derivatives and also the tantalum diaryloxo compound were precursors of the respective cationic compounds [NbCp′Me$_2$X]$^+$ (X = Me, OR) and [TaCp*Me(OR)$_2$]$^+$ after reaction with the Lewis acids E(C$_6$F$_5$)$_3$ (E = B, Al). The cationic niobium complexes were clearly less stable than the related tantalum derivatives, consistent with the lower Lewis acidity of tantalum and also the higher stability of the Ta–C bonds.

Only the aryloxo complex NbCp′Me$_3$(OR) (R = 2,6-Me$_2$C$_6$H$_3$ **2c**) polymerized MMA with low yield when activated with Al(C$_6$F$_5$)$_3$, but not in the presence of B(C$_6$F$_5$)$_3$.

4. Experimental section

4.1. 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 (^{1}H), 376.70 (^{19}F) and 100.60 (^{13}C) MHz on a Bruker AV400. Chemical shifts (δ) are given in parts per million relative to internal TMS (^{1}H and ^{13}C) or external CFCl$_3$ (^{19}F). Elemental analyses were performed on a Perkin–Elmer 240C. Compounds [NbCp′Cl$_4$] [55], [TaCp*Cl$_2$Me$_2$] [56], B(C$_6$F$_5$)$_3$ [57] and 0.5(toluene)·Al(C$_6$F$_5$)$_3$ [39] were prepared by literature methods. MgClMe (3 M in THF), LiMe (1 M in ether) and ROH were purchased from Aldrich. The alcohols were degassed and stored under Ar with molecular sieves (R = tBu, iPr$_3$Si) or sublimed under vacuum (R = 2,6-Me$_2$C$_6$H$_3$). LiOR (R = 2,6-Me$_2$C$_6$H$_3$) was prepared and used *in situ* from reaction of LiBu and ROH in Et$_2$O.

4.2. [NbCp′Me$_4$] (**1**)

MgClMe (4 mL, 3 M in THF) was added to [NbCp′Cl$_4$] (1.120 g, 3.00 mmol) in 60 mL of Et$_2$O at −78 °C. The mixture was then stirred at room temperature for 3 h. The volatiles were removed under vacuum and hexane was added (60 mL) to extract the product. Removal of solvent afforded **1** as a dark oil, which was stored at −20 °C (0.70 g, 80%). ^{1}H NMR (C$_6$D$_6$): 0.04 (s, 9H, Si*Me*$_3$), 1.46 (s, 12H, *Me*Nb), 5.26 (m, 2H, C$_5$*H*$_4$), 5.68 (m, 2H, C$_5$*H*$_4$). ^{13}C {^{1}H} NMR (C$_6$D$_6$): 0.1 (Si*Me*$_3$), 48.9 (*Me*Nb), 110.6, 120.2 (C$_5$*H*$_4$), 1226 (C$_{ipso}$, C$_5$H$_4$). Anal. Calc. for C$_{12}$H$_{25}$NbSi (290.32): C, 49.64; H, 8.68. Found: C, 48.90; H, 8.00.

4.3. [NbCp′Me$_3$(OtBu)] (**2a**)

Compound **1** (0.200 g, 0.69 mmol) and tBuOH (0.051 g, 0.69 mmol) were stirred in toluene for 16 h at ambient temperature. Volatiles were then removed under vacuum, hexane was added (2 × 20 mL) to extract the product, to give **2a** as a brownish oil (0.131 g, 55%). ^{1}H NMR (C$_6$D$_6$): 0.15 (s, 9H, Si*Me*$_3$), 1.01 (s, 6H, *Me*Nb), 1.09 (s, 3H, *Me*Nb), 1.20 (s, 9H, C*Me*$_3$), 5.55 (m, 2H, C$_5$*H*$_4$), 5.63 (m, 2H, C$_5$*H*$_4$). ^{13}C {^{1}H} NMR (C$_6$D$_6$): −0.2 (Si*Me*$_3$), 24.6 (C*Me*$_3$), 42.5 (*Me*Nb), 44.1 (*Me*Nb), 69.8 (*C*Me$_3$), 113.3 (C$_5$*H*$_4$), 113.9 (C$_5$*H*$_4$), 119.3 (C$_{ipso}$, C$_5$H$_4$). Proper analysis of **2a** could not be obtained.

4.4. [NbCp′Me$_3$(OSiiPr$_3$)] (**2b**)

Following the procedure described above, compound **1** (0.200 g, 0.69 mmol) and iPr$_3$SiOH (0.120 g, 0.69 mmol) afforded **2b** as a brownish oil (0.210 g, 68%). ^{1}H NMR (C$_6$D$_6$): −0.16 (s, 9H, Si*Me*$_3$), 1.09 (s, 21H, SiiPr$_2$), 1.19 (s, 6H, *Me*Nb), 1.21 (s, 3H, *Me*Nb), 5.56 (m, 2H, C$_5$*H*$_4$), 5.63 (m, 2H, C$_5$*H*$_4$). ^{13}C {^{1}H} NMR (C$_6$D$_6$): −0.2 (Si*Me*$_3$), 13.6 (CH*Me*$_2$), 18.4 (*C*HMe$_2$), 42.4 (*Me*Nb), 44.4 (*Me*Nb), 113.3 (C$_5$*H*$_4$), 113.6 (C$_5$*H*$_4$), 118.3 (C$_{ipso}$, C$_5$H$_4$). Anal. Calc. for C$_{20}$H$_{43}$NbOSi$_2$ (448.63): C, 53.54; H, 9.66. Found: C, 52.91; H, 9.27.

4.5. [NbCp′Me$_3$(OR)] (R = 2,6-Me$_2$C$_6$H$_3$, **2c**)

In the dry-box an ampoule with a Teflon valve was charged with toluene (20 mL), compound **1** (0.300 g, 1.03 mmol) and ROH (0.126 g, 1.03 mmol) and the solution was heated at 60 °C for 18 h. After this time the solvent was evaporated and the product extracted into hexane (30 mL). Compound **2c** was obtained after elimination of the solvent as a dark oil and was stored at −20 °C (0.36 g, 87%). ^{1}H NMR (C$_6$D$_6$): 0.10 (s, 9H, Si*Me*$_3$), 1.18 (br s, 9H, *Me*Nb), 2.22 (s, 6H, 2,6-*Me*$_2$C$_6$H$_3$), 5.58 (m, 2H, C$_5$*H*$_4$), 5.66 (m, 2H, C$_5$*H*$_4$), 6.78 (m, 1H, *p*-2,6-Me$_2$C$_6$*H*$_3$), 6.92 (m, 2H, *m*-2,6-Me$_2$C$_6$*H*$_3$).

^{13}C {^{1}H} NMR (C$_6$D$_6$): −0.6 (Si*Me*$_3$), 18.2 (2,6-*Me*$_2$C$_6$H$_3$), 46.40 (*Me*Nb), 112.7, 114.8 (C$_5$H$_4$), 118.3 (C$_{ipso}$, C$_5$H$_4$), 122.4 (2,6-Me$_2$C$_6$H$_3$), 128.1 (2,6-Me$_2$C$_6$H$_3$), 129.2 (2,6-Me$_2$C$_6$H$_3$), 158.1 (C$_{ipso}$, 2,6-Me$_2$C$_6$H$_3$). Anal. Calc. for C$_{19}$H$_{31}$NbOSi (396.44): C, 57.56; H, 7.88. Found: C, 57.02; H, 7.77.

4.6. [TaCp*Me$_2$(OR)$_2$] (R = 2,6-Me$_2$C$_6$H$_3$, 3)

2 equiv of LiOR (1.00 mmol) in Et$_2$O (30 mL) was added to a solution of [TaCp*Me$_2$Cl$_2$] (0.20 g, 0.48 mmol) in the same solvent (20 mL) at −78 °C. The final solution was stirred for 16 h at r.t. when the solvent was evaporated to ca. half of the volume and hexane was added (20 mL). The solution was filtered and cooled at −40 °C, yielding 3 as a white solid (0.210 g, 75%). ^{1}H NMR (CDCl$_3$): 0.25 (s, 6H, *Me*Ta), 2.09 (s, 12H, Me$_2$C$_6$H$_3$), 2.12 (s, 15H, C$_5$Me$_5$), 6.63 (m, 2H, p-Me$_2$C$_6$H$_3$), 6.87 (m, 4H, m-Me$_2$C$_6$H$_3$). ^{13}C {^{1}H} NMR (CDCl$_3$): 11.1 (C$_5$Me$_5$), 17.9 (Me$_2$C$_6$H$_3$), 57.1 (*Me*Ta), 119.9 (C$_5$Me$_5$), 121.3 (Me$_2$C$_6$H$_3$), 126.6 (Me$_2$C$_6$H$_3$), 128.5 (Me$_2$C$_6$H$_3$), 158.9 (C$_{ipso}$, 2,6-Me$_2$C$_6$H$_3$). Anal. Calc. for C$_{28}$H$_{39}$O$_2$Ta (588.56); C, 57.14; H, 6.68. Found: C, 57.10; H, 6.58.

4.7. [NbCp′Me$_3$][MeB(C$_6$F$_5$)$_3$] (4)

In the dry-box, a vial was charged with 1 (0.020 g, 0.069 mmol) and B(C$_6$F$_5$)$_3$ (0.038 g, 0.075 mmol) and toluene (2 mL) was then added. After 20 min the formation of oil was observed. The supernatant was decanted and the oily product was washed first with toluene (2 mL) and then with hexane (2 × 2 mL). Compound 4 was obtained as dark oil (0.048 g, 87%). ^{1}H NMR (C$_6$D$_5$Br): −0.09 (s, 9H, Si*Me*$_3$), 1.09 (br s, 3H, B*Me*), 1.51 (br s, 9H, *Me*Nb), 5.81 (m, 2H, C$_5$H$_4$), 5.83 (m, 2H, C$_5$H$_4$). ^{13}C {^{1}H} NMR (C$_6$D$_5$Br): −1.4 (Si*Me*$_3$), 11.5 (*Me*B), 77.5 (*Me*Nb), 112.6 (C$_5$H$_4$), 116.2 (C$_5$H$_4$), 132.2 (C$_{ipso}$, C$_5$H$_4$), 136.4 (C$_6$F$_5$), 137.9 (C$_6$F$_5$), 148.7 (C$_6$F$_5$). ^{19}F NMR (C$_6$D$_5$Br): −131.6 (o-C$_6$F$_5$), −163.4 (p-C$_6$F$_5$), −165.9 (m-C$_6$F$_5$). Adequate elemental analysis could not be obtained for this compound.

4.8. [NbCp′Me$_2$(OSiiPr$_2$)][MeE(C$_6$F$_5$)$_3$] (E = B, 5b-B; Al, 5b-Al)

The same procedure as above from 2b (0.020 g, 0.045 mmol) and B(C$_6$F$_5$)$_3$ (0.027 g, 0.053 mmol) gave 5b-B (0.035 g, 81%). ^{1}H NMR (C$_6$D$_5$Br): −0.04 (s, 9H, Si*Me*$_3$), 0.87 (s, 21H, SiiPr$_2$), 1.14 (s, 3H, *Me*B), 1.42 (s, 6H, *Me*Nb), 6.03 (m, 2H, C$_5$H$_4$), 6.29 (m, 2H, C$_5$H$_4$). ^{13}C {^{1}H} NMR (C$_6$D$_5$Br): −0.9 (Si*Me*$_3$), 11.0 (B*Me*), 12.9 (CH*Me*$_2$), 17.0 (CHMe$_2$), 66.5 (*Me*Nb), 118.1 (C$_5$H$_4$), 120.2 (C$_5$H$_4$), 135.8 (C$_{ipso}$, C$_5$H$_4$), 136.3 (C$_6$F$_5$), 137.9 (C$_6$F$_5$), 148.5 (C$_6$F$_5$). ^{19}F NMR (C$_6$D$_5$Br): −131.6 (o-C$_6$F$_5$), −163.8 (p-C$_6$F$_5$), −166.2 (m-C$_6$F$_5$). Adequate elemental analysis could not be obtained for this compound.

The same procedure as above from 2b (0.020 g, 0.045 mmol) and Al(C$_6$F$_5$)$_3$ (0.031 g, 0.053 mmol) gave 5b-Al (0.034 g, 79%). ^{1}H NMR (C$_6$D$_5$Br): 0.04 (s, 9H, Si*Me*$_3$), 0.21 (br s, 3H, *Me*Al), 0.87 (s, 21H, SiiPr$_2$), 1.42 (s, 6H, *Me*Nb), 6.03 (m, 2H, C$_5$H$_4$), 6.29 (m, 2H, C$_5$H$_4$). ^{13}C {^{1}H} NMR (C$_6$D$_5$Br): −5.7 (Al*Me*), −1.1 (Si*Me*$_3$), 13.0 (CH*Me*$_2$), 17.6 (CHMe$_2$), 66.7 (*Me*Nb), 117.6 (C$_5$H$_4$), 119.8 (C$_5$H$_4$), 118.3 (C$_{ipso}$, C$_5$H$_4$), 136.3 (C$_6$F$_5$), 137.9 (C$_6$F$_5$), 148.5 (C$_6$F$_5$). ^{19}F NMR (C$_6$D$_5$Br): −120.6 (o-C$_6$F$_5$), −158.3 (p-C$_6$F$_5$), −163.3 (m-C$_6$F$_5$). Adequate elemental analysis could not be obtained for this compound.

4.9. [NbCp′Me$_2$(OR)][MeE(C$_6$F$_5$)$_3$] (R = 2,6-Me$_2$C$_6$H$_3$; E = B, 5c-B; Al, 5c-Al)

The same procedure as above for compound 2c (0.020 g, 0.050 mmol) and B(C$_6$F$_5$)$_3$ (0.031 g, 0.060 mmol) afforded 5c-B (0.041 g, 90%). ^{1}H NMR (C$_6$D$_5$Br): −0.15 (s, 9H, Si*Me*$_3$), 1.14 (br s, 3H, B*Me*), 1.58 (br s, 6H, *Me*Nb), 1.87 (s, 6H, 2,6-*Me*$_2$C$_6$H$_3$), 6.09 (m, 2H, C$_5$H$_4$), 6.19 (m, 2H, C$_5$H$_4$), 6.81 (m, 3H, m- and p-2,6-Me$_2$C$_6$H$_3$).

^{13}C {^{1}H} NMR (C$_6$D$_5$Br): −1.2 (Si*Me*$_3$), 11.5 (B*Me*), 17.4 (2,6-Me$_2$C$_6$H$_3$), 69.2 (*Me*Nb), 119.4 (C$_5$H$_4$), 120.5 (C$_5$H$_4$), 128.5 (2,6-Me$_2$C$_6$H$_3$), 128.7 (2,6-Me$_2$C$_6$H$_3$), 128.8 (2,6-Me$_2$C$_6$H$_3$), 131.5 (C$_{ipso}$, C$_5$H$_4$), 136.4 (C$_6$F$_5$), 137.9 (C$_6$F$_5$), 148.7 (C$_6$F$_5$), 161.6 (2,6-Me$_2$C$_6$H$_3$). ^{19}F NMR (C$_6$D$_5$Br): −131.2 (o-C$_6$F$_5$), −163.3 (p-C$_6$F$_5$), −165.8 (m-C$_6$F$_5$). Anal. Calc. for C$_{37}$H$_{31}$BF$_{15}$NbOSi (908.42): C, 48.92; H, 3.44. Found: C, 47.69; H, 3.03.

The same procedure as above for compound 2c (0.020 g, 0.050 mmol) and Al(C$_6$F$_5$)$_3$ (0.032 g, 0.060 mmol) gave 5c-Al (0.039 g, 83%). ^{1}H NMR (C$_6$D$_5$Br, 25 °C): −0.13 (s, 9H, Si*Me*$_3$), 0.21 (br s, 3H, *Me*Al), 1.51 (br s, 6H, *Me*Nb), 1.81 (s, 6H, Me$_2$C$_6$H$_3$), 6.02 (m, 2H, C$_5$H$_4$), 6.11 (m, 2H, C$_5$H$_4$), 6.74 (m, 1H, p-2,6-Me$_2$C$_6$H$_3$), 6.92 (m, 2H, m-2,6-Me$_2$C$_6$H$_3$). ^{13}C {^{1}H} NMR (C$_6$D$_5$Br): −5.5 (Al*Me*), −1.1 (Si*Me*$_3$), 17.4 (Me$_2$C$_6$H$_3$), 67.7 (*Me*Nb), 118.6 (C$_5$H$_4$), 119.8 (C$_5$H$_4$), 128.2 (2,6-Me$_2$C$_6$H$_3$), 128.7 (2,6-Me$_2$C$_6$H$_3$), 128.9 (2,6-Me$_2$C$_6$H$_3$), 130.7 (C$_{ipso}$, C$_5$H$_4$), 136.3 (C$_6$F$_5$), 138.1 (C$_6$F$_5$), 148.4 (C$_6$F$_5$), 161.3 (2,6-Me$_2$C$_6$H$_3$). ^{19}F NMR (C$_6$D$_5$Br): −120.2 (o-C$_6$F$_5$), −157.8 (p-C$_6$F$_5$), −162.7 (m-C$_6$F$_5$). Anal. Calc. for C$_{37}$H$_{31}$AlF$_{15}$NbOSi (924.59): C, 48.06; H, 3.38. Found: C, 47.59; H, 3.13.

4.10. [TaCp*Me(OR)$_2$][MeE(C$_6$F$_5$)$_3$] (R = 2,6-Me$_2$C$_6$H$_3$; E = B, 6-B; E = Al, 6-Al)

The same procedure as above for compound 3 (0.022 g, 0.037 mmol) and B(C$_6$F$_5$)$_3$ (0.023 g, 0.045 mmol) afforded 6-B (0.037 g, 90%). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): 0.46 (br s, 3H, *Me*B), 2.07 (s, 3H, *Me*-Ta), 2.25 (m, 12H, 2,6-*Me*$_2$C$_6$H$_3$), 2.27 (s, 15H, C$_5$Me$_5$), 7.04 (m, 2H, p-2,6-Me$_2$C$_6$H$_3$), 7.12 (m, 4H, m-2,6-Me$_2$C$_6$H$_3$). ^{13}C {^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): 10.1 (B*Me*), 10.4 (C$_5$Me$_5$), 17.4 (Me$_2$C$_6$H$_3$), 52.0 (Ta*Me*), 125.6 (C$_5$Me$_5$), 126.5 (Me$_2$C$_6$H$_3$), 127.7 (Me$_2$C$_6$H$_3$), 129.5 (Me$_2$C$_6$H$_3$), 136.4 (C$_6$F$_5$), 137.9 (C$_6$F$_5$), 148.7 (C$_6$F$_5$), 155.8 (C$_{ipso}$, Me$_2$C$_6$H$_3$). ^{19}F NMR (CD$_2$Cl$_2$): −130.0 (o-C$_6$F$_5$), −162.2 (p-C$_6$F$_5$), −164.7 (m-C$_6$F$_5$). Anal. Calc. for C$_{46}$H$_{39}$BF$_{15}$O$_2$Ta (1100.54): C, 50.20; H, 3.57. Found: C, 49.30; H, 3.08.

The same procedure as above for compound 3 (0.020 g, 0.034 mmol) and Al(C$_6$F$_5$)$_3$ (0.021 g, 0.040 mmol) gave 6-Al (0.033 g, 88%). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): 0.18 (br s, 3H, *Me*Al), 2.05 (s, 3H, *Me*-Ta), 2.28 (s, 12H, Me$_2$C$_6$H$_3$), 2.30 (s, 15H, C$_5$Me$_5$), 7.06 (m, 2H, Me$_2$C$_6$H$_3$), 7.16 (m, 4H, Me$_2$C$_6$H$_3$). ^{13}C {^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): 10.7 (C$_5$Me$_5$), 17.5 (Me$_2$C$_6$H$_3$), 52.3 (Ta*Me*), 125.6 (C$_5$Me$_5$), 125.8 (Me$_2$C$_6$H$_3$), 127.7 (Me$_2$C$_6$H$_3$), 129.2 (Me$_2$C$_6$H$_3$), 136.5 (C$_6$F$_5$), 140.5 (C$_6$F$_5$), 149.9 (C$_6$F$_5$), 155.8 (C$_{ipso}$, Me$_2$C$_6$H$_3$). ^{19}F NMR (CD$_2$Cl$_2$): −120.5 (o-C$_6$F$_5$), −160.0 (p-C$_6$F$_5$), −165.1 (m-C$_6$F$_5$). Anal. Calc. for C$_{46}$H$_{39}$AlF$_{15}$O$_2$Ta (1116.71): C, 49.48; H, 3.52. Found: C, 48.76; H, 3.83.

4.11. Polymerization of MMA

[NbCp′Me$_3$(OR)] (R = 2,6-Me$_2$C$_6$H$_3$ 2c) (0.08 mmol) and Al (C$_6$F$_5$)$_3$ (0.12 mmol) were premixed in 4 mL of toluene in a Teflon-valved ampoule and MMA (1 g, [MMA]:[Ta] = 125:1) was added. The ampoule was stirred at 40 °C. 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$_3$) of the polymer was carried out to determine its tacticity [58]. Gel permeation chromatography (GPC) analyses of polymer samples were carried out in THF at 25 °C (Waters GPCV-2000).

Acknowledgments

Appendix. Supplementary material

Supplementary material associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2010.06.030.

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