

Isolobal Zwitterionic Niobium and Tantalum Imido and Zirconium Monocyclopentadienyl Complexes: Theoretical and Methyl Methacrylate Polymerization Studies

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The trichloro derivatives $[MCl_3(NR)(py)_2]$ reacted with $LiOAr$ to give the imido aryloxo complexes $[MCl_2(NR)(OAr)(py)_2]$ ($M = Nb$, $R = tBu$ (**1a**), Ar (**1b**); $M = Ta$, $R = tBu$ (**2a**); $Ar = 2,6-iPr_2C_6H_3$) and were alkylated with $[BzMgCl]$, affording the tribenzyl derivatives $[NbBz_3(NR)]$ ($R = tBu$ (**3a**), Ar (**3b**)). Similar alkylations of the aryloxo derivatives **1** and **2** gave the dibenzyl complexes $[MBz_2(NR)(OAr)(THF)]$ ($M = Nb$, $R = tBu$ (**5a**); $M = Ta$, $R = tBu$ (**6a**), Ar (**6b**)). The zwitterionic imido complexes $[MBz_2(NtBu)\{\eta^6-C_6H_5CH_2E(C_6F_5)_3\}]$ ($M = Nb$, $E = B$ (**7a-B**), Al (**7a-Al**); $M = Ta$, $E = Al$ (**8a-Al**)) were obtained upon addition of 1 equiv of $E(C_6F_5)_3$ ($E = B, Al$) to the tribenzyl derivatives $[MBz_3(NtBu)]$ ($M = Nb$ (**3a**), Ta (**4a**)). The aryloxo compound **6a** reacted with 2 equiv of the Lewis acids $E(C_6F_5)_3$ ($E = B, Al$) to give the corresponding zwitterionic imido complexes $[TaBz(NtBu)(OAr)\{\eta^6-C_6H_5CH_2E(C_6F_5)_3\}]$ ($E = B$ (**11a-B**), Al (**11a-Al**)) and the adduct $(THF) \cdot E(C_6F_5)_3$, through two different intermediates, the ionic $[TaBz(NtBu)(OAr)(THF)][BzB(C_6F_5)_3]$ (**9a**) for $E = B$ and the neutral $[TaBz_2(NtBu)(OAr)]$ (**10a**) for $E = Al$. The related monocyclopentadienyl complex $[ZrCpBz_2\{\eta^6-C_6H_5CH_2Al(C_6F_5)_3\}]$ (**12-Al**) was also isolated by reaction of $[ZrCpBz_3]$ with $Al(C_6F_5)_3$. DFT calculations were carried out to further understand this type of zwitterionic imido derivative in comparison with the isolobal zirconium cyclopentadienyl compound $[ZrCpBz_2\{\eta^6-C_6H_5CH_2B(C_6F_5)_3\}]$. MMA polymerization was investigated for the $[MBz_2X(NtBu)]/E(C_6F_5)_3$ ($X = Bz, OAr$) and $[ZrCpBz_3]/E(C_6F_5)_3$ ($E = B, Al$) systems.

Introduction

The imido group is a strong π donor ligand with the widely proven ability to stabilize high-valent metal complexes.^{1,2} The isolobal relationship of the imido and the cyclopentadienyl ligands³ is an important feature that allows the half-sandwich imido complexes $[MCp(NR)X_2]$ ($M =$ group 5 metal) to be studied as isoelectronic counterparts of dicyclopentadienyl

derivatives $[MCp_2X_2]$ ($M =$ group 4 metal).^{3–16} The reactivities of these two types of complexes are comparable, although the half-sandwich complexes $[MCp(NR)X_2]$ ($M =$ group 5 metal) were rather less active olefin polymerization catalysts than the metallocene-type complexes $[MCp_2X_2]$ ($M =$ group 4 metal).^{17–19} This difference has been attributed to the lower acidity of group 5 metal derivatives, which would consequently be expected to show a greater affinity for polar olefins. Conversely, important differences between these two types of complexes involve the reactivity of the metal–nitrogen multiple bond.^{13,20–23}

Control of the stereochemistry and polydispersity of the polymer chain and the production of well-defined block

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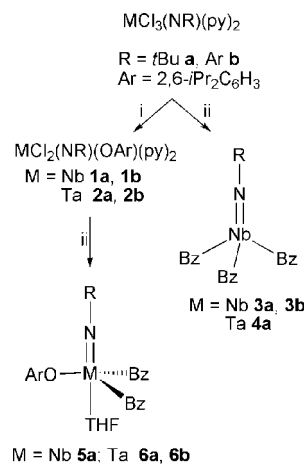
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copolymers^{24–30} are essential features of the polymerization of methacrylates by transition-metal complexes. Group 3 and 4 metallocene complexes have been widely explored over the past few years and, more recently,^{24–36} tantalum cyclopentadienyl based complexes have also emerged as active catalysts for MMA polymerization.^{17,37,38} Different mechanisms based on group transfer polymerization have been proposed, involving mono-nuclear or dinuclear alkyl or enolate active species and depending on the cocatalyst employed, mainly $E(C_6F_5)_3$ ($E = B, Al$). However, MMA polymerization has also been described for group 4 imido metallocene complexes in the presence of $Al(C_6F_5)_3$, involving the formation of an oxametallacycle by addition of MMA to the metal–nitrogen multiple bond and further generation of a zwitterionic dinuclear enol aluminate intermediate by rupture of the metal–oxygen bond produced by $Al(C_6F_5)_3$.³⁹

In this work, we have extended our initial interest in half-sandwich imido neutral $[MCp(NR)X_2]$ ($M = \text{group 5 metal}$)^{9–14,40–44} and cationic monocyclopentadienyl group 5 metal complexes^{45,46} to noncyclopentadienyl imido complexes of the type $[MBz_2(NR)X]$ ($M = Nb, Ta; X = Bz, OAr$), with the aim of synthesizing cationic derivatives by reaction with the Lewis acids $E(C_6F_5)_3$ ($E = B, Al$) and exploring their activity as MMA polymerization catalysts. Initial studies related to the tribenzyl compounds ($X = Bz$) have also been extended to the aryloxo derivatives ($X = OAr$) in order to modify their reactivity and to stabilize these types of high-valent cationic compounds.

Scheme 1^a

^aLegend: (i) LiOAr; (ii) BzMgCl.

Recently, Bergman et al. have reported the synthesis of the tantalum tribenzyl derivative $[Ta(NrBz)_3]$,⁴⁷ which in the presence of the Lewis acids $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ generates the corresponding zwitterionic and ion-unpaired derivatives that were applied as catalysts for the hydroamination of acetylenes.

Furthermore, considering the isolobal relationship between the imido and cyclopentadienyl ligands,¹ a similar relation could be established between the non-cyclopentadienyl imido complexes $[MX_3(NR)]$ ($M = \text{group 5 metal}$) and monocyclopentadienyl complexes $[MCpX_3]$ ($M = \text{group 4 metal}$). This last type of complex has found widespread application as an olefin polymerization catalyst, including MMA,^{25,48} and thus comparative chemical and DFT studies have also been carried out in this work.

Results and Discussion

Synthesis of Neutral Compounds. Following the procedure previously reported by Wigley et al. for the synthesis of $[TaCl_2(NAr)(OAr)(py)_2]$ ($Ar = 2,6\text{-}iPr_2C_6H_3$)⁴⁹ by reaction of the trichloro complexes with LiOAr, we have isolated the new imido aryloxo compounds $[MCl_2(NR)(OAr)(py)_2]$ ($M = Nb, R = tBu$ (**1a**), Ar (**1b**); $M = Ta, R = tBu$ (**2a**)) in good yields, using the respective trichloro imido derivatives $[MCl_3(NR)(py)_2]$ ($M = Nb, R = tBu, Ar$; $M = Ta, R = tBu$)^{49,50} as source materials (Scheme 1). All of these new complexes retained the original two molecules of pyridine coordinated to the metal center, whichever imido substituent was used.

The trichloro imido compounds $[NbCl_3(NR)(py)_2]$ ($R = tBu, Ar$) and the aryloxo imido compounds **1** and **2a** were transformed into the benzyl derivatives $[NbBz_3(NR)]$ ($R = tBu$ (**3a**), Ar (**3b**)) and $[MBz_2(NR)(OAr)(THF)]$ ($M = Nb, R = tBu$ (**5a**); $M = Ta, R = tBu$ (**6a**), Ar (**6b**)), respectively, after addition of the corresponding molar amounts of $[BzMgCl]$ (Scheme 1). The synthesis of the aryloxo complexes **5a** and **6a** required addition of stoichiometric amounts of $[BzMgCl]$ to prevent formation of the corresponding tribenzyl derivatives $[MBz_3(NR)]$, which

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were observed when working with an excess resulting from the simultaneous substitution of the aryloxo group. This side reaction could be responsible for the lower yields obtained in the synthesis of complexes **5a** and **6** with respect to those observed for complexes **3** and [TaBz₃(NtBu)]⁴⁷ (**4a**). The yields of these reactions also reflected the different electronic stabilizations provided by the two different types of imido groups. When R was *t*Bu, the yields were moderate to good, whereas rather poor yields were obtained when R was Ar and in the particular case of the complexes [TaCl₃(NAr)(py)₂] and [NbCl₂(NAr)(OAr)(THF)] (**1b**) none of the benzyl derivatives could be observed.

The ¹H and ¹³C NMR spectra of the tribenzyl imido compounds **3a,b** showed only one resonance for the three equivalent benzyl ligands. The ¹J_{C-H} value of the methylene group (ca. 133 Hz) and the chemical shift of the ipso carbon of the phenyl ring (δ ~138) suggested η² coordination of the benzyl ligand,^{47,51,52} which was confirmed by X-ray diffraction studies (vide infra). The same spectroscopic parameters were observed for the tantalum complex [TaBz₃(NtBu)] (**4a**).⁴⁷

The elemental analysis of **5a** and **6a,b** were consistent with the proposed chemical formulas, and their ¹H and ¹³C NMR spectra demonstrated coordination of THF to a metal center bound to two equivalent benzyl ligands, with the diastereotopic methylene protons observed as a pair of doublets in the ¹H NMR spectrum. The ¹J_{C-H} value of the methylene group (ca. 120 Hz) and the chemical shift of the ipso carbon (δ ~145) of the benzyl ligands were consistent with their η¹ coordination. These structural features are consistent with a trigonal-bipyramidal geometry in which the strong donor imido and THF ligands occupy the axial positions, whereas the aryloxo and two benzyl ligands are located in the equatorial positions. This structure was supported by the results of NOE experiments.

The metal centers of these imido complexes show different coordination numbers. The trichloro and dichloroaryloxo derivatives **1** and **2a** are 18-electron pseudooctahedral compounds with two additional pyridine ligands, considering the aryloxo and imido ligands as 3- and 4-electron donors, respectively. However, considering the benzyl ligand as a 1-electron donor, the dibenzylaryloxo derivatives **5a** and **6** with one additional THF molecule are 16-electron trigonal bipyramidal species and the ligand-free neutral tribenzyl **3** and **4a** are 12-electron compounds with a pseudotetrahedral geometry.

Surprisingly, neither the steric hindrance nor the strong σ and π donor character of the aryloxo ligand in the imido complexes **5** and **6a** prevented the coordination of one additional neutral THF ligand, whereas the tribenzyl imido complexes **3** and **4a** did not coordinate additional ligands. Furthermore, the *cis* coordination of the imido and aryloxo ligands was expected to maximize the overlapping of the π orbitals of these ligands with the metal center.⁴⁹ Apparently, the σ donating ability and the η² coordination of the three benzyl groups weaken the interaction of the metal center with the neutral donor ligand in compounds **3** and **4a**, facilitating the dissociation of this ligand, which is removed after washing with hexane and drying under vacuum for a few hours.

X-ray Structure of 3a. Crystals suitable for X-ray diffraction studies were obtained for the tribenzyl imido compound [NbBz₃(NtBu)] (**3a**). The molecular structure of **3a** is shown in Figure 1, and a selection of bond distances and angles is

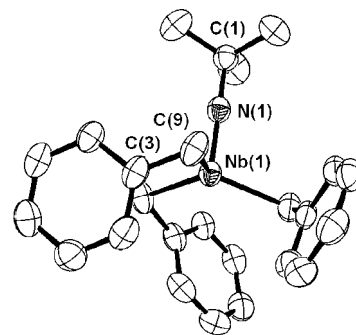


Figure 1. ORTEP diagram of [NbBz₃(NtBu)] (**3a**). Hydrogen atoms have been omitted, and thermal ellipsoids are shown at the 50% level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Compounds [MBz₃(NtBu)] (M = Nb (**3a**), Ta⁴⁷)

	M = Nb	M = Ta
M–N	1.747(4)	1.737(6)
M–C(9)	2.245(3)	2.216(4)
M–C(3)	2.679(3)	2.678
M–N–C(1)	180.00(1)	180.00
M–C(3)–C(9)	89.62(17)	90.80(3)
N–M–C(9)	98.26(9)	100.0(1)
C(9)–M–C(9)	117.97(4)	117.06(7)

presented in Table 1. Complex **3a** exhibits a C_{3v} pseudotetrahedral structure, which resembles that found in typical monocyclopentadienyl three-legged piano-stool derivatives, with three narrower N–Nb–C and three more open C–Nb–C angles. The bond length and bond angle values were very close to those found in the analogous tantalum derivative [TaBz₃(NtBu)] (Table 1). The three Nb–C_{ipso} distances (2.679(3) Å) and the three Nb–C–C_{ipso} angles (89.62(2)°) are clearly indicative of η²-benzyl coordination. Although this η² interaction is well represented for electron-deficient metal–benzyl compounds,^{53–59} the presence of three equivalent η²-benzyl ligands is unusual, probably as a consequence of the coordinative requirements of the metal atom, in comparison with those of the related zirconium cyclopentadienyl derivative [ZrCpBz₃].⁶⁰ Finally, the Nb–N bond distance (1.747(4) Å) is in the range expected for a Nb–N triple bond, in accordance with the linearity observed for the Nb–N–C bond angle (180.00(1)°).¹

Synthesis of Zwitterionic Compounds. The reactions of the tribenzyl derivatives [MBz₃(NtBu)] (M = Nb (**3a**), Ta (**4a**)) with the Lewis acids E(C₆F₅)₃ (E = B, Al) afforded the zwitterionic compounds [MBz₂(NtBu){η⁶-C₆H₅CH₂E(C₆F₅)₃}] (M = Nb, E = B (**7a-B**), Al (**7a-Al**); M = Ta, E = Al (**8a-Al**)) (Scheme 2). All of these new complexes were soluble in C₆D₆. Formation of the hypothetical niobium compounds [NbBz₂(NAr){η⁶-C₆H₅CH₂E(C₆F₅)₃}] in similar reactions with the arylimido

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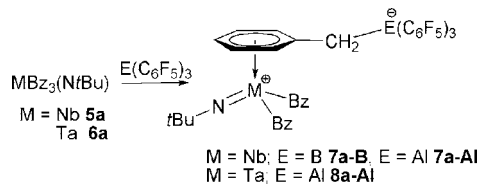
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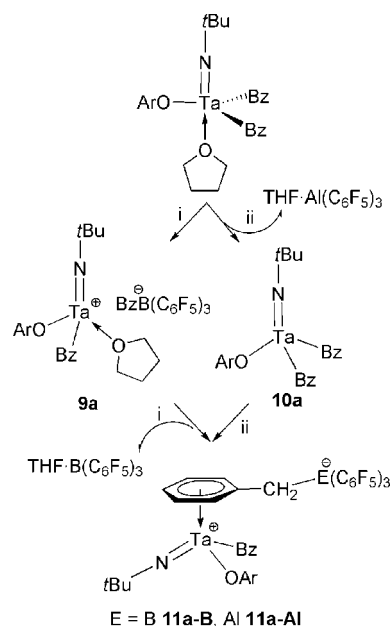
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Scheme 2. Reaction of Tribenzyl Imido Complexes with the Lewis Acids E(C₆F₅)₃ (E = B, Al)


derivative **3b** were unsuccessful, in accordance with the σ -donor capacity of the aryloxo ligand being lesser than that of the related *tert*-butylimido ligand.

The ¹H and ¹³C NMR spectra of complexes **7** and **8** showed similar patterns which were also analogous to that reported for [TaBz₂(N*t*Bu){ η^6 -C₆H₅CH₂B(C₆F₅)₃}] (**8a-B**).⁴⁷ The C_s symmetry of complexes **7** and **8** gave rise to the three resonances observed in the ¹H NMR spectra for the AA'BB'C spin system of the η^6 -C₆H₅ ring and the two doublets for the diastereotopic M-CH₂ protons of the two equivalent benzyl ligands. The values found for ¹J_{C-H} of the benzyl methylene group and for the chemical shift of the ipso carbon atom of the phenyl ring were very close to those found for the starting [MBz₃(N*t*Bu)] complexes, indicating a similar η^2 coordination. Formation of the [C₆H₅CH₂E(C₆F₅)₃][−] anion moiety was indicated by a broad signal observed at about 3 ppm for the Bz-E groups. Coordination of the anionic benzylborate phenyl ring to the metal center was in agreement with the upfield shift of three resonances with respect to those expected for a normal phenyl ring, although such displacement was not observed for the related zirconium complexes [ZrCpBz₂{ η^6 -C₆H₅CH₂E(C₆F₅)₃}] (E = B,⁶¹ Al (vide infra)). We believe that this different behavior could be attributed to slippage of the phenyl ring in complexes **7** and **8**, as has been confirmed by the DFT calculations discussed below. Finally, the presence of the ion-pair interaction for the benzylborate complex **7a-B** was confirmed by means of the $\delta_{\text{meta}}-\delta_{\text{para}}$ difference of about 4 ppm observed in its ¹⁹F NMR spectrum.

In addition, the reactivity toward Lewis acids was studied for the aryloxo imido compounds [MBz₂(NR)(OAr)(THF)] (M = Nb, R = *t*Bu (**5a**); M = Ta, R = *t*Bu (**6a**), Ar (**6b**)). However, only the tantalum derivative **6a** reacted successfully with the Lewis acids E(C₆F₅)₃ (E = B, Al) (Scheme 3). Addition of 1 equiv of B(C₆F₅)₃ to a C₆D₆ solution of **6a** gave an insoluble reddish oil, which after being redissolved in BrC₆D₅ was characterized by NMR spectroscopy as the ionic compound [TaBz(N*t*Bu)(OAr)(THF)][BzB(C₆F₅)₃] (**9a**). The ¹H NMR of **9a** showed one broad resonance for the methylene protons of the benzyl-B group at about δ 3.20, two multiplets due to the coordinated THF, and two doublets corresponding to the methylene protons CH₂-Nb of the niobium-bonded benzyl group. In addition, three resonances due to the [BzB(C₆F₅)₃][−] anion were observed in the ¹⁹F NMR spectrum with a value of 2.8 ppm for the $\delta_{\text{meta}}-\delta_{\text{para}}$ difference, indicating that the ion-pair interaction⁶² does not exist. Addition of another 1 equiv of B(C₆F₅)₃ to **9a** produced the abstraction of THF, leading to formation of the zwitterionic complex [TaBz(N*t*Bu)(OAr){ η^6 -C₆H₅CH₂B(C₆F₅)₃}] (**11a-B**), with elimination of the (THF)·B(C₆F₅)₃ adduct and concomitant η^6 coordination of the C₆H₅ ring of the [BzB(C₆F₅)₃][−] anion. The same transformation

Scheme 3. Reaction of Dibenzy Aryloxo Imido Complexes with the Lewis Acids E(C₆F₅)₃ (E = B, Al)^a


^aLegend: (i) B(C₆F₅)₃; (ii) Al(C₆F₅)₃.

directly into **11a-B** can be obtained by addition of 2 equiv of B(C₆F₅)₃ to the starting compound **6a**.

The first step of the similar reaction of **6a** with Al(C₆F₅)₃ was the elimination of the neutral (THF)·Al(C₆F₅)₃ adduct with formation of the neutral THF-free tantalum complex [TaBz₂(NR)(OAr)] (**10a**), which was also characterized by NMR spectroscopy. Clearly, the higher oxophilicity of Al vs B was responsible for this different reaction pathway. Furthermore, the formation of the THF-free compound **10a** from **6a** demonstrated that coordination of the THF ligand stabilizes the aryloxo compounds **5** and **6** with respect to the less electron-deficient tribenzyl derivatives **3** and **4**, although it is not an essential requirement for their isolation. This fact could suggest that the benzyl ligand is a better σ donor ligand than the aryloxo ligand. The ¹H and ¹³C NMR spectroscopic data of **10a** were very close to those observed for **6a**, with slight shifts of the whole set of resonances. Addition of another 1 equiv of Al(C₆F₅)₃ produced the abstraction of one of the benzyl ligands to give the corresponding zwitterionic compound [TaBz(N*t*Bu)(OAr){ η^6 -C₆H₅CH₂Al(C₆F₅)₃}] (**11a-Al**), which showed a ¹H and ¹³C NMR pattern similar to that observed for **11a-B**. Furthermore, the three resonances corresponding to the [η^6 -C₆H₅CH₂Al(C₆F₅)₃][−] anion at δ −121.6 (F_{ortho}), −149.9 (F_{para}), and −159.4 (F_{meta}) were observed in the ¹⁹F NMR spectrum.

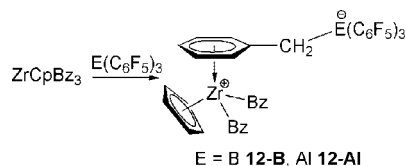
In contrast to the ionic compound **9a** containing the free borate anion, the new zwitterionic compounds **11a-B** and **11a-Al** were soluble in C₆D₆. The interaction proposed for the [η^6 -C₆H₅CH₂E(C₆F₅)₃][−] anions (E = B, Al) in both complexes was confirmed by the upfield shifted C₆H₅ resonances observed in their ¹H NMR spectra. Furthermore, the ¹⁹F NMR spectrum of **11a-B** showed a higher value of ca. 4.0 ppm for the $\delta_{\text{meta}}-\delta_{\text{para}}$ difference, in accordance with the presence of a strong ion-pairing interaction,⁶² whereas three resonances corresponding to the [η^6 -C₆H₅CH₂Al(C₆F₅)₃][−] anion at δ −121.6 (F_{ortho}), −149.9 (F_{para}), and −159.4 (F_{meta}) were observed in the ¹⁹F NMR spectrum of **11a-Al**.

The reactivity described here for these group 5 metal imido complexes resembles that reported for the zirconium derivative

(61) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473.

(62) Horton, A. D.; de With, J.; van der Linden, A. J.; van der Weg, H. *Organometallics* **1996**, *15*, 2672.

Scheme 4. Reaction of the Zirconium Tribenzyl Monocyclopentadienyl Complex with Lewis Acids $E(C_6F_5)_3$ ($E = B, Al$)



[ZrCpBz₃], which also yielded the analogous zwitterionic η^6 -arene compound [ZrCpBz₂{ η^6 -C₆H₅CH₂B(C₆F₅)₃}] (**12-B**), when reacting with B(C₆F₅)₃.⁶¹ In view of these results, we decided to complete our previous studies investigating the related reaction of [ZrCpBz₃] with Al(C₆F₅)₃ (Scheme 4). The reaction was carried out in C₆D₆ and monitored by NMR spectroscopy at ambient temperature to give the expected zwitterionic complex [ZrCpBz₂{ η^6 -C₆H₅CH₂Al(C₆F₅)₃}] (**12-Al**), which was characterized by NMR spectroscopy. The ¹H spectrum showed broad signals resulting from the formation of **12-Al**, and the ¹⁹F NMR spectrum presented three resonances corresponding to the [η^6 -C₆H₅CH₂Al(C₆F₅)₃][−] anion. However, the ¹H NMR spectrum obtained from a similar experiment in CD₂Cl₂ at −70 °C clearly showed three multiplets corresponding to the η^6 -coordinated phenyl ring of the benzylborate anion and two doublets for the diastereotopic methylene protons of the metal-bound benzyl ligands. The most remarkable difference from the related group 5 metal compounds is that the ¹J_{C–H} value of the Zr–CH₂ group (122 Hz) and the chemical shift of the phenyl ipso carbon of this benzyl ligand (δ 148.5) show the typical values expected for η^1 -coordinated benzyl ligands in contrast to the η^2 interaction found for the group 5 metal imido derivatives **7** and **8**, probably due to the bulkiness of the cyclopentadienyl ligand.

Theoretical Calculations. Optimized geometries of the most stable conformers for the complexes [NbMe₂(*Nt*Bu){ η^6 -C₆H₅CH₂B(C₆F₅)₃}] (**I**) and [ZrMe₂Cp{ η^6 -C₆H₅CH₂B(C₆F₅)₃}] (**II**) are shown in Figure 2, and calculated values of bond distances and angles are collected in Table 2. These complexes are models for the zwitterionic compounds [NbBz₂(*Nt*Bu){ η^6 -C₆H₅CH₂B(C₆F₅)₃}] (**7a-B**) and [ZrCpBz₂{ η^6 -C₆H₅CH₂B(C₆F₅)₃}] (**12-B**), respectively, where the benzyl groups were replaced by methyl ligands. The complexes show a pseudotetrahedral arrangement of ligands around the metal center. The calculated Nb–N distance (1.743 Å) and Nb–N–C angle (180.0°) are consistent with a Nb≡N triple bond, and they are essentially the same as those experimentally found for the similar complex **3a** (1.748 Å and 180.0° in Figure 1, respectively). The spatial orientation of the arene ligand with respect to the metal fragment in both complexes can be defined using the N–Nb–X–C1 and X2–Zr–X1–C1 dihedral angles (where X stands for the centroid of the different rings). As can be seen in Figure 2, the spatial positions of the arene ligand are roughly the same for both complexes (64.8 and 64.1° for complexes **I** and **II**, respectively). The distance between the metal atom and the arene centroid is slightly longer for complex **II** (2.302 versus 2.269 Å). The Nb–C_{arene} distances can be grouped in two sets, one with short distances Nb–C1, Nb–C2, and Nb–C3 (2.646, 2.521, and 2.567 Å, respectively) and other set of long distances Nb–C4, Nb–C5, and Nb–C6 (2.721, 2.814, and 2.742 Å, respectively). However, the Zr–C_{arene} distances are closer to each other. Furthermore, the standard deviation of the distances between the metal center and the carbon atoms belonging to the arene ligand (0.111 and 0.026 Å for complexes **I** and **II**, respectively) indicate a less symmetric coordination of the arene

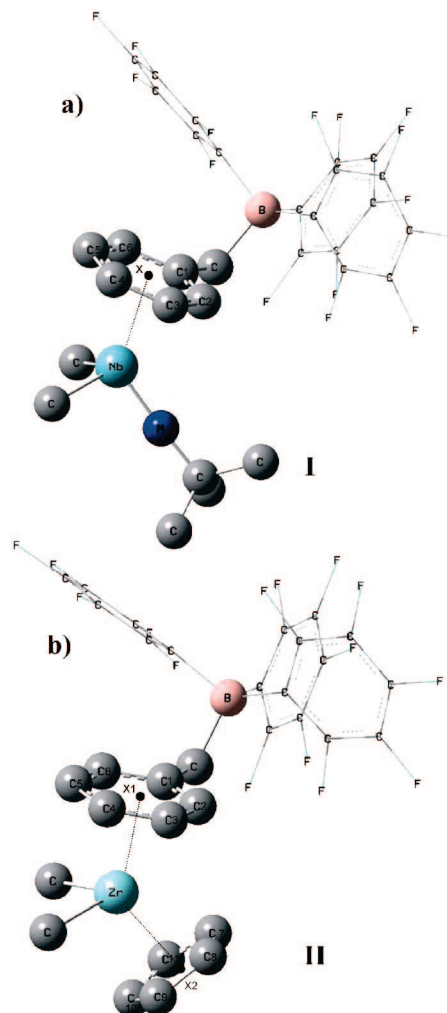


Figure 2. DFT-optimized geometries of the complexes (a) [NbMe₂(*Nt*Bu){ η^6 -C₆H₅CH₂B(C₆F₅)₃}] (**I**) and (b) [ZrMe₂Cp{ η^6 -C₆H₅CH₂B(C₆F₅)₃}] (**II**).

Table 2. Calculated Values of Bond Distances (Å) and Angles (deg) of the Complexes [NbMe₂(*Nt*Bu){ η^6 -C₆H₅CH₂B(C₆F₅)₃}] (**I**) and [ZrMe₂Cp{ η^6 -C₆H₅CH₂B(C₆F₅)₃}] (**II**)^a

	M = Nb	M = Zr	M = Zr ^b
Nb–N	1.742		
Zr–X2		2.200	2.180
M–Me	2.166	2.258	
	2.170	2.260	
M–X1	2.269	2.302	2.300
M–C1	2.646	2.719	2.860
M–C2	2.521	2.668	2.730
M–C3	2.567	2.663	2.610
M–C4	2.721	2.702	2.663
M–C5	2.814	2.726	2.680
M–C6	2.742	2.707	2.740
C–B	1.690	1.687	1.690
C1–B	1.470	1.472	1.490
C1–C–B	113.8	114.2	112.0
X1–Zr–X2		133.1	126.0
N–Nb–X	126.5		
X2–Zr–X1–C1		64.1	
N–Nb–X–C1	64.8		

^a X stands for the position of the centroid in the corresponding ring, X1 for η^6 -C₆H₅CH₂B, and X2 for η^5 -C₅H₅. ^b Experimental values for [ZrBz₂Cp{ η^6 -C₆H₅CH₂B(C₆F₅)₃}].⁶¹

ligand to the metal fragment for complex **I** with respect to complex **II**. In Table 2, a comparison of the geometry of

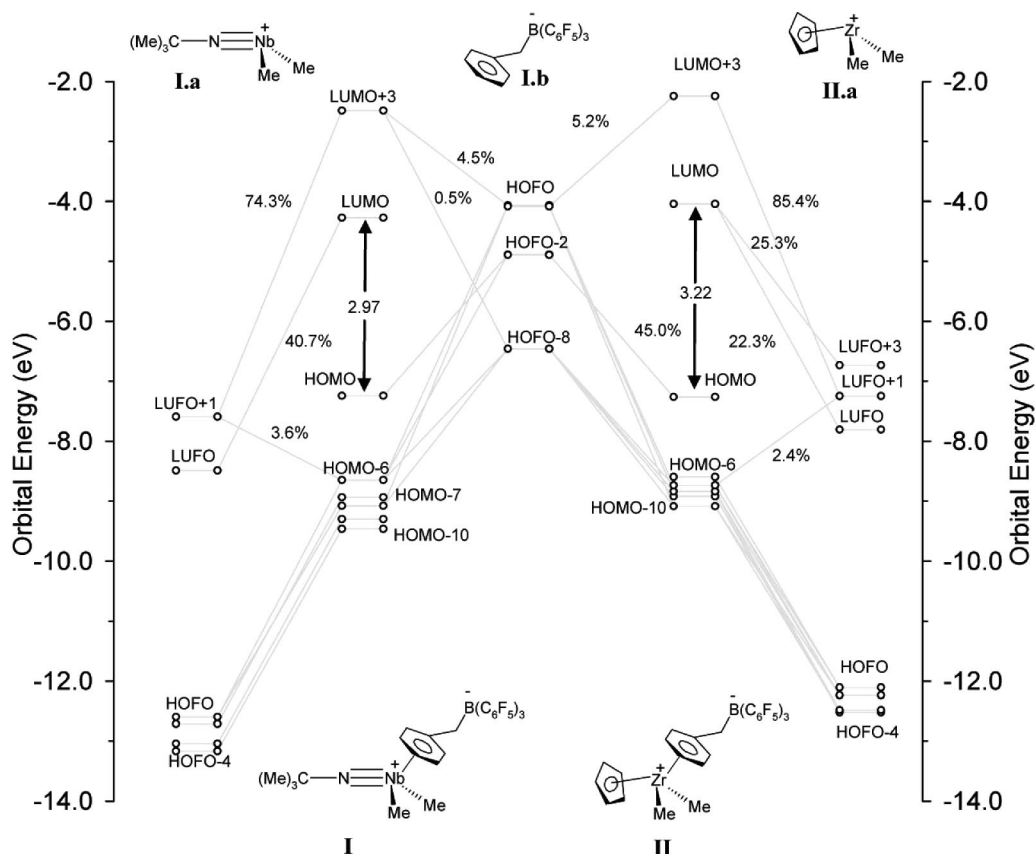


Figure 3. Molecular orbital diagram for the formation of complexes **I** and **II** from the corresponding fragments.

complex **II** and the structure obtained by Pellecchia et al. for the zwitterionic complex $[\text{ZrBz}_2\text{Cp}\{\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3\}]$ is given.⁶¹ In general, the experimental and calculated structures are quite similar; only differences of around 0.1 Å and 5° in distances and angles, respectively, are observed.

Frontier Orbitals of Complexes I and II. In order to gain further insight into the metal–ligand bonding, a fragment molecular orbital approach is applied to establish the frontier orbitals of complexes **I** and **II**. Thus, the $[\text{NbMe}_2(\text{NtBu})\{\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3\}]$ complex (**I**) can be seen as being formed by two different fragments, the cationic fragment $[\text{NbMe}_2(\text{NtBu})]^+$ (**I.a**) and the anionic fragment $[\text{C}_6\text{H}_5\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3]^-$ (**I.b**), respectively. Similarly, $[\text{ZrMe}_2\text{Cp}\{\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3\}]$ complex (**II**) is made from the component fragments $[\text{ZrCpMe}_2]^+$ (**II.a**) and $[\text{C}_6\text{H}_5\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3]^-$ (**I.b**), respectively.

The LUFO (lowest unoccupied fragment orbital) and LUFO+1 from fragment **I.a** are essentially pure d_{z^2} and $d_{x^2-y^2}$ orbitals from the metal, respectively. Other unoccupied LUFOs for **I.a** are antibonding π^* orbitals arising from the interaction between d_{xz} , d_{yz} , and d_{xy} metal orbitals and occupied π orbitals of the imido group, fundamentally p_x , p_y , and p_z orbitals from the nitrogen atom. The corresponding occupied π orbitals for the metal–imido bond, HOFO, HOFO+1, and HOFO+3 (highest occupied fragment orbital), show a clear bonding character arising from the interaction between Nb d and N p atomic orbitals. Frontier molecular orbitals for the **II.a** fragment are quite similar to those in fragment **I.a**. The HOFO and HOFO+1 orbitals for the **I.b** fragment have π^* character on the benzyl ring.

A simplified molecular orbital correlation diagram is depicted in Figure 3. The isolobal and isoelectronic character of both complexes is clear, although some differences are observed. The LUMO orbital for complex **I** arises mainly from the interaction

between the empty LUFO **I.a** (40.7%), which is mainly a d_{z^2} orbital, and LUFO+3 **I.b** (11.9%) with a small contribution of the HOFO **I.b** (2.0%). The total Mulliken overlap population for this orbital is $-0.008e$ which indicates a slightly antibonding character for this MO. For complex **II**, the corresponding LUMO orbital rises from mixing LUFO+3 **II.a** ($d_{x^2-y^2}$, 22.3%) and LUFO **II.a** (d_{z^2} , 25.3%) with the LUFO+3 **I.b** (17.3%) orbital but without the participation of the HOFO **I.b**. The Mulliken overlap population for the LUMO of complex **II** has a value of $0.055e$. In contrast, LUMO orbital energies in both complexes are rather similar (-4.27 and -4.04 eV for complexes **I** and **II**, respectively). Hence, a donor molecule might yield a more stable donor–acceptor bond in complex **II** due to the bonding character of the LUMO orbital.

Another important ligand-to-metal interaction between the fragments defined above in both complexes arises from the interaction between HOFO **I.a** (HOFO **I.b**), LUFO+1 **I.a** (LUFO **I.b**), and HOFO **I.b** orbitals giving predominantly the LUMO+3 and HOMO-6 molecular orbitals in complexes **I** (**II**). The character of LUMO+3 is strongly antibonding for both complexes ($-0.220e$ and $-0.516e$ for complexes **I** and **II**, respectively), while for HOMO-6 a slightly antibonding character is observed ($-0.016e$ and $-0.005e$ for complexes **I** and **II**, respectively), probably due to the repulsive interaction between HOMO orbitals of the two fragments. The interaction between the HOFO and HOFO-8 of fragment **I.b** with HOFO-0–HOFO-4 for both metal fragments gives an increase in energy (destabilization) of the molecular orbital responsible of Nb–imido and Zr–Cp bonds (HOMO-7–HOMO-10 set in Figure 3).

Finally, the total Mulliken overlaps for complexes **I** and **II** are positive ($0.240e$ and $0.208e$, respectively,) pointing to a stable interaction between fragments.

Table 3. Polymerization of MMA with Imido Complexes using E(C₆F₅)₃ (E = B, Al) as Cocatalyst^a

run	[M]	E	T (°C)	t (h)	yield (%)	M _w /M _n ^b	10 ⁴ M _n	10 ⁴ M _n (calcd) ^c	rr (%) ^d	mr (%) ^d	mm (%) ^d
1	3a	Al	−40	5	37	1.25	2.03	0.76	60	34	6
2 ^e	3a	Al	0	5	30	2.08	2.93	0.76	72	27	2
3	3a	Al	0	5	40	1.28	2.01	0.76	62	33	7
4	3a	Al	25	16	50	1.35	2.01	1.04	70	23	7
5	6a	B	25	16	14	1.47	5.21	0.29	61	32	7
6	6a	Al	40	5	10	1.47	3.84	0.21	58	33	9

^a Polymerization conditions: Complex [M] (4.8 × 10^{−5} mol) and E(C₆F₅)₃ (9.6 × 10^{−5} mol) premixed in toluene (3 mL), then MMA (1 g; [MMA]:[M] = 206:1). ^b Determined by GPC in THF vs polystyrene standards. ^c M_n(calcd) values = conv × [MMA]/[M] × 100.81 (100.81 is the formula weight of MMA); ^d Determined by ¹H NMR in CDCl₃. ^e CH₂Cl₂.

Formation Energies for Complexes I and II. Electronic formation energies of the complexes **I** and **II**, with respect to the isolated fragments, are −117.0 and −113.8 kcal/mol, reflecting the exergonic nature of the bond between them. The stabilization energy for complex **I** is 3.2 kcal/mol higher than that corresponding to complex **II**, indicating a more difficult separation of the ionic pair for complex **I** with respect to complex **II**.

MMA Polymerization. The niobium tribenzyl imido complex [NbBz₃(N*t*Bu)] (**3a**) activated by addition of 2.0 equiv of Al(C₆F₅)₃ showed rather low catalytic activity for MMA polymerization, whereas only traces of PMMA were observed when the isolobal zirconium derivative [ZrCpBz₃] was used for comparison and when the related niobium imido (**3b**) and tantalum imido (**4**) complexes were studied under similar conditions. In contrast, no activation was observed for any of these compounds when B(C₆F₅)₃ was used as the Lewis acid. The catalytic activity of complex **3a** was variable at different times and temperatures, the best result being obtained at 25 °C for 16 h with a moderate yield of PMMA (run 4). Shorter periods of time and lower temperatures (Table 3, runs 1 and 3) gave lower yields, being significantly much lower when the time was shorter than 5 h. However, periods of time longer than 16 h did not improve the yield, and even lower yields were obtained at temperatures higher than 25 °C, indicating the decomposition of the active species with both time and temperature. The polymers obtained were mainly syndiotactic, with higher syndiotacticity under the conditions corresponding to run 3. When CH₂Cl₂ instead of toluene was employed as the solvent, the polymer obtained was also syndiotactic (over 70%) but in a lower yield and with a higher polydispersity (run 2 vs 3), probably as a consequence of the instability of the Nb–C and Al–C bonds in this solvent. In contrast, the only tantalum aryloxo benzyl derivative isolated, **6a**, showed catalytic activity with both Lewis acids (run 5 and 6), but again with rather poor yields of syndiotactic PMMA.

Activation of **3a** by Al(C₆F₅)₃ but not by B(C₆F₅)₃ suggests either the formation of an enolate species by benzyl transfer to a MMA · Al(C₆F₅)₃ adduct^{37,63} or the [4 + 2] addition of MMA to the metal–imido bond, generating a metallacycle.³⁹ In the case of the neutral complexes **3–6** presented in this work, none of them reacted with MMA. Furthermore, we monitored the reaction of MMA · Al(C₆F₅)₃ with **3a** in C₆D₆ by NMR spectroscopy, obtaining a mixture of two compounds. Although we have not been able to characterize these compounds, the *t*Bu ¹³C resonances at δ 71.8 and δ 72.4 confirmed the presence of the imido moiety, in agreement with benzyl transfer to the MMA · Al(C₆F₅)₃ adduct. Unfortunately, the ¹⁹F NMR spectrum did not allow us to determine the presence of the corresponding enol aluminate anions, due to the number of resonances.

The lesser donor capacity of the NAr imido ligand may explain the lack of activity of **3b**, in agreement with the easy decomposition observed when it was reacted with E(C₆F₅)₃. The different activities for MMA polymerization shown by the niobium complex **3a** and the zirconium complex [ZrCpBz₃] could be related to the greater kinetic inertness of the Zr–benzyl bond in [ZrCpBz₃]. Finally, the activation of **6a** by B(C₆F₅)₃ suggests that in this case the tantalum center is responsible for the polymerization activity.

Conclusions

Benzylation with [BzMgCl] of the niobium trichloro imido complexes [NbCl₃(NR)(py)₂] (R = *t*Bu, Ar; Ar = 2,6-*i*Pr₂C₆H₃) previously reported and of the new niobium and tantalum dichloro imido derivatives [MCl₂(NR)(OAr)(py)₂] (M = Nb, Ta; R = *t*Bu, Ar) gave the corresponding benzyl complexes [NbBz₃(NR)] and [MBz₂(NR)(OAr)(THF)], respectively. The resulting yields depended on the donor capacity of the imido ligand, being moderate to good for the *tert*-butyl but low for the aryl derivatives. The lower σ donor ability of the aryloxo group compared with the benzyl ligand was also responsible for the coordination of one additional THF ligand to give the trigonal-bipyramidal pentacoordinate aryloxo complexes.

One of the benzyl groups of the new isolated imido compounds was abstracted by the Lewis acids E(C₆F₅)₃ (E = B, Al) generating the stable zwitterionic complexes [MBz₂–(N*t*Bu){η⁶–C₆H₅CH₂E(C₆F₅)₃}] (M = Nb, Ta; E = B, Al) and [TaBz(N*t*Bu)(OAr){η⁶–C₆H₅CH₂E(C₆F₅)₃}] (E = B, Al) containing the η⁶-coordinated phenyl ring of the benzylborate anion. When these reactions were carried out with imido complexes containing O- and C-donor competing ligands (THF and benzyl, respectively), abstraction of THF by the more oxophilic Al(C₆F₅)₃ Lewis acid was the preferred first step of the reaction, whereas the benzyl ligand was first abstracted by the less oxophilic B(C₆F₅)₃ reagent. Formation of similar zwitterionic compounds was studied by reactions of the zirconium derivative [ZrCpBz₃] with the same Lewis acids E(C₆F₅)₃ (E = B,⁴⁷ Al).

DFT calculations showed that the cationic fragments [NbMe₂(N*t*Bu)]⁺ and [ZrCpMe₂]⁺ and the zwitterionic compounds [NbMe₂(N*t*Bu){η⁶–C₆H₅CH₂B(C₆F₅)₃}] (**I**) and [ZrMe₂Cp{η⁶–C₆H₅CH₂B(C₆F₅)₃}] (**II**) were isolobal and isoelectronic, respectively. However, both theoretical and NMR data showed a small difference in the coordination of the η⁶-benzyl ligand to the niobium atom with respect to the zirconium compound. The antibonding character of the LUMO orbital in complex **I** shows an unfavorable reaction with donor monomers. However, the LUMO orbital in complex **II** has a remarkable bonding character, producing stable interactions with donor ligands. Reactions which imply separation of the ionic pair should be more difficult for complex **I**, due to the higher stabilization energy compared with complex **II**.

Polymerization of methyl methacrylate was achieved with moderate yield for the catalytic system [NbBz₃(N*t*Bu)]/Al(C₆F₅)₃

(63) Rodríguez-Delgado, A.; Chen, E. Y. X. *Macromolecules* **2005**, *38*, 2587.

and with low yields for the systems [TaBz(NrBu)(OAr)(THF)]/E(C₆F₅)₃ (E = B, Al); meanwhile, the zirconium monocyclopentadienyl derivative [ZrCpBz₃] only produced traces of PMMA. Two main reasons can be advanced for these results: the reactivity of the metal–imido bond toward unsaturated systems which could interfere with polymerization and the kinetic inertness of the metal–benzyl bond with respect to the usually more active metal–methyl bonds, although we have not been able to isolate this last type of compound. Further studies aimed at a better understanding of the polymerization process are in progress.

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 (¹⁹F), and 100.60 (¹³C) MHz on a Bruker AV400. Chemical shifts (δ) are given in ppm using C₆D₆ as solvent, unless otherwise stated. ¹H and ¹³C resonances were measured relative to solvent peaks considering TMS at 0 ppm; meanwhile ¹⁹F resonances were measured relative to external CFCl₃. Assignment of resonances was made from HMQC and HMBC NMR experiments. Elemental analyses were performed on a Perkin-Elmer 240C. The compounds [TaCl₂(NAr)(OAr)(py)₂],⁴⁹ [MCl₃(NR)(py)₂] (M = Nb, Ta; R = *t*Bu, Ar),^{49,50} B(C₆F₅)₃,⁶⁴ and Al(C₆F₅)₃·0.5(toluene)¹⁷ were prepared by literature methods.

[NbCl₂(NrBu)(OAr)(py)₂] (1a; Ar = 2,6-*i*Pr₂C₆H₃). LiOAr·THF (0.60 g, 2.33 mmol) in Et₂O/THF (20 mL/10 mL) was added to a solution of [NbCl₃(NrBu)(py)₂] (1.00 g, 2.33 mmol) in Et₂O/THF (15:5 mL) at 25 °C. The reaction mixture was stirred for a further 16 h. The resulting yellow solution was separated by filtration, and the volatiles were removed under reduced pressure. The residue was washed with hexane (3 × 15 mL) and then dried to give **1a** as a yellow solid (1.06 g, 80%). ¹H NMR: 1.24 (s, 9H, CMe₃), 1.44 (d, *J* = 6.9 Hz, 12H, Me₂CH), 4.46 (sept, *J* = 6.9 Hz, 2H, Me₂CH), 6.45 (m, 4H, *m*-py), 6.75 (m, 2H, *p*-py), 7.05 (m, 1H, *p*-C₆H₃), 7.25 (m, 2H, *m*-C₆H₃), 9.14 (m, 4H, *o*-py). ¹³C NMR: 24.3 (Me₂CH), 26.4 (Me₂CH), 30.3 (CMe₃), 68.5 (CMe₃), 121.9 (*p*-C₆H₃), 123.6 (*m*-C₆H₃), 123.7 and 127–6 (*m*-py), 137.3 (*o*-C₆H₃), 137.8 and 137.9 (*p*-py), 151.9 and 152.8 (*o*-py), 162.0 (*i*-C₆H₃). Anal. Calcd for C₂₆H₃₆Cl₂N₃NbO (569.13): C, 54.75; H, 6.36; N, 7.37. Found: C, 55.42; H, 6.20; N, 7.42.

[NbCl₂(NAr)(OAr)(py)₂] (1b; Ar = 2,6-*i*Pr₂C₆H₃). Following the same methodology described above, complex **1b** was obtained from the reaction of [NbCl₃(NAr)(py)₂] (1.00 g, 1.88 mmol) in 20 mL of Et₂O/THF (2/1) with LiOAr·THF (0.48 g, 1.88 mmol) in 30 mL of Et₂O/THF (2/1) as a yellow solid (1.01 g, 80%). ¹H NMR: 1.25 (m, 24H, Me₂CH), 4.33 (m, 4H, Me₂CH), 6.28–6.50 (m, 8H, py), 7.00 (m, 2H, *p*-C₆H₃), 7.05 (m, 4H, *m*-C₆H₃), 8.80 (m, 4H, *o*-C₆H₃), 9.10 (m, 2H, *o*-py). ¹³C NMR: 24.3, 24.8 (Me₂CH), 26.1, 28.0 (Me₂CH), 122.4, 122.9, 123.6, 124.3, 125.67, 137.6, 138.1, 147.2, 150.8, 152.6 (C₆H₃ and py), 151.3 (*i*-C₆H₃N), 160.4 (*i*-C₆H₃O). Anal. Calcd for C₃₄H₄₀Cl₂N₃NbO (670.51): C, 60.90; H, 6.01; N, 6.27. Found: C, 60.66; H, 5.85; N, 6.42.

[TaCl₂(NrBu)(OAr)(py)₂] (2a; Ar = 2,6-*i*Pr₂C₆H₃). Following the same methodology described above, complex **2a** was obtained from the reaction of [TaCl₃(NrBu)(py)₂] (1.00 g, 1.52 mmol) in 20 mL of Et₂O/THF (2/1) with LiOAr·THF (0.50 g, 1.93 mmol) in 30 mL of Et₂O/THF (2/1) as a yellow solid (1.01 g, 80%). ¹H NMR: 1.31 (s, 9H, CMe₃), 1.44 (d, *J* = 6.9 Hz, 12H, Me₂CH), 4.41 (sept, *J* = 6.9 Hz, 2H, Me₂CH), 6.36 and 6.51 (m, 4H, *m*-py), 6.69 and 6.79 (m, 2H, *p*-py), 7.04 (m, 1H, *p*-C₆H₃), 9.11 (m, 4H, *o*-py), 7.28 (m, 2H, *m*-C₆H₃). ¹³C NMR: 24.5 (Me₂CH), 26.3 (Me₂CH), 32.4 (CMe₃), 68.1 (CMe₃), 121.7 (*p*-C₆H₃), 123.6 (*m*-C₆H₃), 123.9 and

124.3 (*m*-py), 137.8 and 138.2 (*p*-py), 137.9 (*o*-C₆H₃), 151.2 and 153.3 (*o*-py), 160.0 (*i*-C₆H₃). Anal. Calcd for C₂₆H₃₆Cl₂N₃OTa (658.44): C, 47.43; H, 5.51; N, 6.38. Found: C, 47.20; H, 5.46; N, 6.39.

[NbBz₃(NrBu)] (3a). BzMgCl (2 M in THF, 6.99 mmol) was added to a solution of [NbCl₃(NrBu)(py)₂] (1.00 g, 2.33 mmol) in 20 mL of Et₂O at –78 °C. The resulting yellow mixture was stirred for 16 h at 25 °C, after which the solution was filtered over Celite and the volatiles were removed. The solid product was washed with pentane and dried in vacuo, yield 0.81 g (80%). ¹H NMR: 1.35 (s, 9H, CMe₃), 1.68 (s, 6H, CH₂Ph), 6.57 (m, 3H, C₆H₅), 6.98 (m, 12H, C₆H₅). ¹³C NMR: 31.8 (CMe₃), 53.3 (CH₂Ph), 125.4 (*p*-C₆H₅), 129.4 (*m*-C₆H₅), 130.1 (*o*-C₆H₅), 136.0 (*i*-C₆H₅), the *i*-CMe₃ resonance was not observed. Anal. Calcd for C₂₅H₃₀NNb (437.42): C, 68.65; H, 6.91; N, 3.20. Found: C, 68.50; H, 6.87; N, 3.20.

[NbBz₃(NAr)] (3b; Ar = 2,6-*i*Pr₂C₆H₃). The same procedure described for **3a** was followed, using [NbCl₃(NAr)(py)₂] (1.00 g, 1.88 mmol) in 20 mL of Et₂O and BzMgCl (2 M in THF, 5.54 mmol), affording **3b** as a clear yellow solid (0.22 g, 25%). ¹H NMR: 1.34 (d, *J* = 6.9 Hz, 12H, Me₂CH), 1.90 (s, 6H, CH₂Ph), 4.20 (sept, *J* = 6.9 Hz, 2H, Me₂CH), 6.62 (m, 3H, C₆H₅), 7.00–7.20 (m, 15H, C₆H₃, C₆H₅). ¹³C NMR: 24.4 (Me₂CH), 26.3 (Me₂CH), 28.4 (CH₂Ph), 123.0, 124.5, 126.2, 128.5, 128.8, 130.3, (C₆H₃, C₆H₅), 134.9 (*i*-C₆H₅), 144.9 (*i*-C₆H₃). Anal. Calcd for C₃₃H₃₈NNb (541.57): C, 73.19; H, 7.07; N, 3.59. Found: C, 73.25; H, 7.07; N, 2.53.

[NbBz₂(NrBu)(OAr)(THF)] (5a; Ar = 2,6-*i*Pr₂C₆H₃). BzMgCl (2 M in THF, 1.40 mmol) was added to a stirred solution of [NbCl₂(NAr)(OAr)(py)₂] (**1b**; 0.40 g, 0.70 mmol) in 30 mL of Et₂O at –78 °C. The reaction slurry was stirred for 16 h at 25 °C, and then 10 mL of hexane was added. The solution was filtered, and the volatiles were removed at reduced pressure to give **5a** as a yellow solid (0.12 g, 30%). ¹H NMR: 0.92 (s, 9H, CMe₃), 1.31 (d, *J* = 6.9 Hz, 12H, Me₂CH), 1.36 (m, 4H, β-CH₂, THF), 1.96 (d, *J* = 10.0 Hz, 2H, CH₂Ph), 2.94 (d, *J* = 10.0, 2H, CH₂Ph), 3.46 (sept, *J* = 6.9 Hz, 2H, Me₂CH), 3.70 (m, 4H, α-CH₂, THF), 6.98–7.20 (m, 13H, C₆H₃ and C₆H₅). ¹³C NMR: 23.3 (Me₂CH), 25.3 (β-CH₂, THF), 27.1 (Me₂CH), 31.3 (CMe₃), 69.1 (α-CH₂, THF), 69.2 (CH₂Ph), 121.3, 123.1, 123.9, 128.9, 129.1, 135.7 (C₆H₃, C₆H₅), 144.0 (*i*-C₆H₅), 162.1 (*i*-C₆H₃); the *i*-CMe₃ resonance was not observed. Anal. Calcd for C₃₄H₄₈NNbO₂ (595.66): C, 68.56; H, 8.12; N, 2.35. Found: C, 68.80; H, 8.20; N, 2.10.

[TaBz₂(NrBu)(OAr)(THF)] (6a; Ar = 2,6-*i*Pr₂C₆H₃). The same procedure described above for **5a** was followed using [TaCl₂(NrBu)(OAr)(py)₂] (0.40 g, 0.60 mmol) and BzMgCl (2 M in THF, 1.21 mmol) to give **6a** as a yellow solid (0.14 g, 35%). ¹H NMR: 0.92 (s, 9H, CMe₃), 1.29 (d, *J* = 6.9 Hz, 12H, Me₂CH), 1.30 (m, 4H, β-CH₂, THF), 1.90 (d, *J* = 11.4 Hz, 2H, CH₂Ph), 2.74 (d, *J* = 11.4 Hz, 2H, CH₂Ph), 3.44 (sept, *J* = 6.9 Hz, 2H, Me₂CH), 3.66 (m, 4H, α-CH₂, THF), 6.96–7.12 (m, 13H, C₆H₃ and C₆H₅). ¹³C NMR: 23.5 (Me₂CH), 25.4 (β-CH₂, THF), 27.3 (Me₂CH), 32.6 (CMe₃), 66.0 (CMe₃), 69.5 (α-CH₂, THF), 121.8, 123.2, 123.5, 129.6, 129.9, 135.9 (C₆H₃, C₆H₅), 146.0 (*i*-C₆H₅), 160.6 (*i*-C₆H₃). Anal. Calcd for C₃₄H₄₈NO₂Ta (683.70): C, 59.73; H, 7.08; N, 2.05. Found: C, 60.02; H, 7.42; N, 2.09.

[TaBz₂(NAr)(OAr)(THF)] (6b; Ar = 2,6-*i*Pr₂C₆H₃). The same procedure described for **5a** was followed using [TaCl₂(NAr)(OAr)(py)₂] (0.40 g, 0.52 mmol) and BzMgCl (2 M in THF, 1.04 mmol), giving complex **6b** as an orange solid (0.080 g, 20%). ¹H NMR: 1.25 (m, 24H, Me₂CH), 1.30 (m, 4H, β-CH₂, THF), 2.80 (m, 4H, CH₂Ph), 3.57 (m, 4H, α-CH₂, THF), 3.91 (sept, *J* = 6.6 Hz, Me₂CH), 4.10 (sept, *J* = 6.5 Hz, 2H, Me₂CH), 6.08–7.18 (m, 16H, C₆H₃ and C₆H₅). We were not able to obtain an adequate elemental analysis for compound **6b**.

[NbBz₂(NrBu){η⁶-C₆H₅CH₂B(C₆F₅)₃}] (7a-B). In a glovebox, C₆D₆ solutions of the compounds [NbBz₃(NrBu)] (**3a**; 0.017 g, 0.034 mmol) and B(C₆F₅)₃ (0.015 g, 0.034 mmol) were loaded into

an NMR tube. The reaction was followed by NMR spectroscopy, resulting in the immediate formation of complex **7a-B** (100%). The solution was layered with hexane to give a microcrystalline yellow solid (0.018 g, 50%). ^1H NMR: 0.80 (s, 9H, CMe_3), 1.02 (d, $J = 9.0$ Hz, 2H, PhCH_2Nb), 1.74 (d, $J = 9.0$ Hz, 2H, PhCH_2Nb), 3.28 (m, 2H, PhCH_2B), 5.44 (m, 1H, $p\text{-C}_6\text{H}_5\text{CH}_2\text{B}$), 5.67 (m, 2H, $m\text{-C}_6\text{H}_5\text{CH}_2\text{B}$), 6.34 (m, 4H, $o\text{-C}_6\text{H}_5\text{CH}_2\text{Nb}$), 6.49 (m, 2H, $o\text{-C}_6\text{H}_5\text{CH}_2\text{B}$), 6.84 (m, 4H, $m\text{-C}_6\text{H}_5\text{CH}_2\text{Nb}$), 6.98 (m, 2H, $p\text{-C}_6\text{H}_5\text{CH}_2\text{Nb}$). ^{13}C NMR: 30.6 (CMe_3), 36.0 (CH_2B), 45.7 (CH_2Nb), 71.2 (CMe_3), 117.2 ($p\text{-C}_6\text{H}_5\text{CH}_2\text{B}$), 122.9 ($o\text{-C}_6\text{H}_5\text{CH}_2\text{B}$), 126.2 ($m\text{-C}_6\text{H}_5\text{CH}_2\text{B}$), 128.4 ($\text{C}_6\text{H}_5\text{CH}_2\text{Nb}$), 129.6 ($\text{C}_6\text{H}_5\text{CH}_2\text{Nb}$), 131.2 ($i\text{-C}_6\text{H}_5\text{CH}_2\text{Nb}$), 136.5 (C_6F_5), 138.9 (C_6F_5), 148.0 (C_6F_5). ^{19}F NMR: -129.5 (m, 6F, $o\text{-C}_6\text{F}_5$), -159.2 (m, 3F, $p\text{-C}_6\text{F}_5$), -163.4 (m, 6F, $m\text{-C}_6\text{F}_5$). Anal. Calcd for $\text{C}_{43}\text{H}_{30}\text{BF}_{15}\text{NNb}$ (949.40): C, 54.40; H, 3.18; N, 1.48. Found: C, 54.13; H, 3.00; N, 1.29.

[NbBz₂(NBu){ $\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{Al}(\text{C}_6\text{F}_5)_3$ }] (7a-Al). The same procedure described for **7a-B** was followed using **[NbBz₃(NBu)]** (**3a**; 0.017 g, 0.034 mmol) and $\text{Al}(\text{C}_6\text{F}_5)_3$ (0.017 g, 0.034 mmol), resulting in the immediate formation of complex **7a-Al** (100% by ^1H NMR). ^1H NMR: 0.71 (s, 9H, CMe_3), 0.84 (d, $J = 8.7$ Hz, 2H, PhCH_2Nb), 1.83 (d, $J = 8.7$ Hz, 2H, PhCH_2Nb), 2.76 (m, 2H, PhCH_2Al), 5.21 (m, 1H, $p\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 5.81 (m, 2H, $m\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 6.24 (m, 4H, $o\text{-C}_6\text{H}_5\text{CH}_2\text{Nb}$), 6.30 (m, 2H, $o\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 6.81 (m, 4H, $m\text{-C}_6\text{H}_5\text{CH}_2\text{Nb}$), 6.99 (m, 2H, $p\text{-C}_6\text{H}_5\text{CH}_2\text{Nb}$). ^{13}C NMR: 30.8 (CMe_3), 33.9 (PhCH_2Al), 47.7 (CH_2Nb), 70.9 (CMe_3), 110.4 ($p\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 120.6 ($o\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 124.9 ($m\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 128.5 ($\text{C}_6\text{H}_5\text{CH}_2\text{Nb}$), 129.3 ($\text{C}_6\text{H}_5\text{CH}_2\text{Nb}$), 129.7 ($\text{C}_6\text{H}_5\text{CH}_2\text{Nb}$), 130.9 ($\text{C}_6\text{H}_5\text{CH}_2\text{Nb}$), 137.2 (C_6F_5), 141.2 (C_6F_5), 150.4 (C_6F_5), 159.6 (C_6F_5). ^{19}F NMR: -119.9 (m, 6F, $o\text{-C}_6\text{F}_5$), -153.5 (m, 3F, $p\text{-C}_6\text{F}_5$), -160.8 (m, 6F, $m\text{-C}_6\text{F}_5$).

[TaBz₂(NBu){ $\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{Al}(\text{C}_6\text{F}_5)_3$ }] (8a-Al). The same procedure described for **7a-B** was followed using **[TaBz₃(NBu)]** (**4a**; 0.016 g, 0.028 mmol) and $\text{Al}(\text{C}_6\text{F}_5)_3$ (0.015 g, 0.028 mmol), resulting in the immediate formation of complex **8a-Al** (100% by ^1H NMR). ^1H NMR: 0.80 (s, 9H, CMe_3), 0.98 (d, $J = 10.5$ Hz, 2H, PhCH_2Ta), 1.69 (d, $J = 10.5$ Hz, 2H, PhCH_2Ta), 2.83 (m, 2H, PhCH_2Al), 5.18 (m, 1H, $p\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 5.80 (m, 2H, $m\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 6.29 (m, 2H, $o\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 6.43 (m, 4H, $o\text{-C}_6\text{H}_5\text{CH}_2\text{Ta}$), 6.84 (m, 4H, $m\text{-C}_6\text{H}_5\text{CH}_2\text{Ta}$), 7.10 (m, 2H, $p\text{-C}_6\text{H}_5\text{CH}_2\text{Ta}$). ^{13}C NMR: 32.0 (CMe_3), 34.0 (PhCH_2Al), 50.7 (PhCH_2Ta), 68.1 (CMe_3), 109.6 ($p\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 120.4 ($o\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 125.0 ($m\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 128.9 ($\text{C}_6\text{H}_5\text{CH}_2\text{Ta}$), 129.7 ($\text{C}_6\text{H}_5\text{CH}_2\text{Ta}$), 131.7 ($\text{C}_6\text{H}_5\text{CH}_2\text{Ta}$), 133.7 ($\text{C}_6\text{H}_5\text{CH}_2\text{Ta}$), 139.1 (C_6F_5), 150.1 (C_6F_5), 160.7 (C_6F_5). ^{19}F NMR: -120.9 (m, 6F, $o\text{-C}_6\text{F}_5$), -154.3 (m, 3F, $p\text{-C}_6\text{F}_5$), -161.7 (m, 6F, $m\text{-C}_6\text{F}_5$).

[TaBz(NtBu)(OAr)(THF)][BzB(C₆F₅)₃] (9a; Ar = 2,6-*i*Pr₂-C₆H₃). $\text{B}(\text{C}_6\text{F}_5)_3$ (0.011 g, 0.022 mmol) was added to a solution of compound **6a** (0.015 g, 0.022 mmol) in C_6D_6 . The precipitation of an oil was immediately observed. This was then separated from the C_6D_6 solution and dissolved in $\text{C}_6\text{D}_5\text{Br}$. The NMR spectra of the solution at 25 °C showed the formation of complex **9a**. ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$): 1.08 (s, 9H, CMe_3), 1.10 (d, $J = 6.7$ Hz, 12H, Me_2CH), 1.33 (m, 4H, $\beta\text{-CH}_2$, THF), 1.50 (m, 2H, PhCH_2Ta), 3.27 (m, 2H, PhCH_2B), 3.43 (m, 2H, Me_2CH), 3.83 (m, 4H, $\alpha\text{-CH}_2$, THF), 6.70–7.10 (m, 13H, C_6H_3 and C_6H_5). ^{13}C NMR ($\text{C}_6\text{D}_5\text{Br}$): 23.4 (Me_2CH), 25.6 (Me_2CH), 26.4 ($\beta\text{-CH}_2$, THF), 32.0 (PhCH_2B), 33.6 (CMe_3), 65.0 ($\alpha\text{-CH}_2$, THF), 68.7 (CMe_3), 74.8 ($\text{PhCH}_2\text{-Ta}$), 123.2, 124.6, 125.3, 127.5, 129.4, 132.5, 149.3, (C_6H_3 , C_6H_5), 137.6 ($i\text{-C}_6\text{H}_5$), 154.7 ($i\text{-C}_6\text{H}_3$), 126.7 (C_6F_5), 129.6 (C_6F_5), 131.5 (C_6F_5). ^{19}F NMR ($\text{C}_6\text{D}_5\text{Br}$): -128.9 (m, 6F, $o\text{-C}_6\text{F}_5$), -162.3 (m, 3F, $p\text{-C}_6\text{F}_5$), -165.2 (m, 6F, $m\text{-C}_6\text{F}_5$).

[TaBz₂(NBu)(OAr)] (10a; Ar = 2,6-*i*Pr₂-C₆H₃). $\text{Al}(\text{C}_6\text{F}_5)_3$ (0.012 g, 0.022 mmol) was added to a solution of compound **6a** (0.015 g, 0.022 mmol) in C_6D_6 . The reaction was monitored by NMR spectroscopy to determine the formation of complex **10a** and the adduct $\text{THF} \cdot \text{Al}(\text{C}_6\text{F}_5)_3$. ^1H NMR: 0.98 (m, 4H, $\beta\text{-CH}_2$, THF), 1.12 (s, 9H, CMe_3), 1.20 (d, $J = 6.9$ Hz, 12H, Me_2CH), 1.87 (d, $J =$

$= 11.4$ Hz, 2H, PhCH_2), 2.61 (d, $J = 11.4$ Hz, 2H, PhCH_2), 3.40 (m, 6H, Me_2CH and $\alpha\text{-CH}_2$, THF), 6.90–7.15 (m, 18H, C_6H_3 and C_6H_5). ^{13}C NMR: 23.5 (Me_2CH), 24.9 (Me_2CH), 27.1 ($\beta\text{-CH}_2$, THF), 33.8 (CMe_3), 65.1 ($\alpha\text{-CH}_2$, THF), 67.5 (CMe_3), 73.8 (CH_2Ph), 122.9, 123.3, 125.3, 125.6, 128.5, 129.3, 129.5, 129.7, 136.9, 147.1 (C_6H_3 , C_6H_5), 139.8 ($i\text{-C}_6\text{H}_5$), 158.4 ($i\text{-C}_6\text{H}_3$), 137.1 (C_6F_5), 142.0 (C_6F_5), 150.0 (C_6F_5).

[TaBz(NtBu)(OAr){ $\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{E}(\text{C}_6\text{F}_5)_3$ }] (E = B (11a-B**), Al (**11a-Al**); Ar = 2,6-*i*Pr₂-C₆H₃).** In a glovebox, C_6D_6 solutions of compounds **6a** (0.015 g, 0.022 mmol) and $\text{E}(\text{C}_6\text{F}_5)_3$ (E = B, Al; 0.044 mmol), were added to a Teflon-valved NMR tube. The reaction was monitored by NMR spectroscopy to determine the formation of compounds **11a-E** and the adducts $\text{THF} \cdot \text{E}(\text{C}_6\text{F}_5)_3$. Complex **11a-B**: ^1H NMR 1.10 (m, 4H, $\beta\text{-CH}_2$, THF), 1.18 (m, 21H, Me_2CH and CMe_3), 2.33 (d, $J = 8.7$ Hz, 1H, PhCH_2Ta), 3.24 (m, 6H, $\alpha\text{-CH}_2$, THF and PhCH_2B), 3.46 (m, 2H, Me_2CH), 3.62 (d, $J = 8.7$ Hz, 1H, PhCH_2Ta), 6.20–7.20 (m, 13H, C_6H_3 and C_6H_5); ^{13}C NMR 22.9 (Me_2CH), 23.1 (Me_2CH), 27.3 ($\beta\text{-CH}_2$, THF), 29.0 (PhCH_2B), 32.9 (CMe_3), 59.0 ($\alpha\text{-CH}_2$, THF), 76.0 (PhCH_2Ta), 123.3, 123.5, 124.8, 125.6, 126.3, 129.3, 130.5, 131.5, 136.4, 146.3 (C_6H_3 , C_6H_5), 141.6 ($i\text{-C}_6\text{H}_5$), 152.0 ($i\text{-C}_6\text{H}_3$), 137.3 (C_6F_5), 144.8 (C_6F_5), 148.5 (C_6F_5), the $i\text{-CMe}_3$ resonance was not observed; ^{19}F NMR -130.2 (m, 6F, $o\text{-C}_6\text{F}_5$), -154.2 (m, 3F, $p\text{-C}_6\text{F}_5$), -161.4 (m, 6F, $m\text{-C}_6\text{F}_5$). Complex **11a-Al**: ^1H NMR 0.98 (m, 4H, $\beta\text{-CH}_2$, THF), 1.16 (m, 12H, Me_2CH), 1.19 (s, 9H, CMe_3), 2.34 (d, $J = 8.7$ Hz, 1H, PhCH_2Ta), 3.20 (m, 2H, PhCH_2Al), 3.43 (m, 6H, Me_2CH and $\alpha\text{-CH}_2$, THF), 3.62 (d, $J = 8.7$ Hz, 1H, PhCH_2Ta), 6.10–7.20 (m, 18H, C_6H_3 , C_6H_5). ^{13}C NMR: 23.4 (Me_2CH), 24.8 (Me_2CH), 27.0 ($\beta\text{-CH}_2$, THF), 29.0 (PhCH_2Al), 33.0 (CMe_3), 65.0 ($\alpha\text{-CH}_2$, THF), 67.2 (CMe_3), 74.0 (PhCH_2Ta), 122.8, 123.2, 125.2, 125.5, 128.4, 129.1, 129.4, 129.6, 131.2, 136.2, 136.8, 137.7, 142.4, 146.9 (C_6H_3 , C_6H_5), 139.6 ($i\text{-C}_6\text{H}_5$), 158.3 ($i\text{-C}_6\text{H}_3$), 137.2 (C_6F_5), 142.0 (C_6F_5), 150.5 (C_6F_5); ^{19}F NMR -123.3 (m, 6F, $o\text{-C}_6\text{F}_5$), -151.5 (m, 3F, $p\text{-C}_6\text{F}_5$), -161.1 (m, 6F, $m\text{-C}_6\text{F}_5$).

[Zr($\eta^5\text{-C}_5\text{H}_5$)Bz₂{ $\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{Al}(\text{C}_6\text{F}_5)_3$ }] (12-Al). In a glovebox, C_6D_6 solutions of the compounds **[ZrCpBz₃]** (0.018 g, 0.042 mmol) and $\text{Al}(\text{C}_6\text{F}_5)_3$ (0.042 mmol) were mixed in a Teflon-valved NMR tube. The reaction was followed by NMR spectroscopy, and the formation of compound **12-Al** was observed (100% by ^1H NMR). ^1H NMR: 1.48 (d, $J = 11$ Hz, 2H, PhCH_2Zr), 1.59 (d, $J = 11$ Hz, 2H, PhCH_2Zr), 2.64 (b.s., 2H, PhCH_2Al), 5.21 (s, 5H, C_5H_5), 5.58 (b.s., 1H, $p\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 5.80 (br s, 2H, $m\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 6.16 (br s, 2H, $o\text{-C}_6\text{H}_5\text{CH}_2\text{Al}$), 6.80–7.20 (m, 15H, $\text{C}_6\text{H}_5\text{CH}_2$ and $\text{C}_6\text{H}_5\text{Me}$). ^{19}F NMR: -119.9 (m, 6F, $o\text{-C}_6\text{F}_5$), -154.5 (m, 3F, $p\text{-C}_6\text{F}_5$), -161.4 (m, 6F, $m\text{-C}_6\text{F}_5$).

X-ray Structure Determination of 3a (C₂₅H₃₀NNb, $M_r = 437.41$). Single crystals of **3a** suitable for the X-ray diffraction study were grown from hexane. A yellow crystal was selected, covered with perfluorinated ether and mounted on a Bruker-Nonius Kappa CCD single-crystal diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Data collection was performed at 200(2) K: crystal dimensions $0.22 \times 0.18 \times 0.16$ mm, trigonal crystal system, space group $P3_1c$, $a = 11.2683(13)$ Å, $c = 10.2514(11)$ Å, $V = 1127.3(2)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.289$ g cm⁻³, $F(000) = 456$, 9387/1724 collected/unique reflections ($R(\text{int}) = 0.0868$), θ range $3.62\text{--}27.49^\circ$. Multiscan⁶⁵ absorption correction procedures were applied to the data ($\mu = 0.542$ mm⁻¹, minimum/maximum transmission 0.749/0.918). The structure was solved, using the WINGX package,⁶⁶ by direct methods (SHELXS-97) and refined by using full-matrix least squares against F^2 (SHELXL-97).⁶⁷ All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms. Full-matrix least-squares refinements were carried

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out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/error <0.001. The final cycle of full-matrix least-squares refinement based on 1724 reflections and 82 parameters converged to final values of $R1(F^2 > 2\sigma(F^2)) = 0.0327$, $wR2(F^2 > 2\sigma(F^2)) = 0.0557$, $R1(F^2) = 0.0497$, $wR2(F^2) = 0.0593$. Final difference Fourier maps showed no peaks higher than 0.190 e Å⁻³ or deeper than -0.284 e Å⁻³. CCDC-655227 (**3a**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Methods. All energies and geometries were calculated using the B3P86 hybrid DFT method as implemented in Gaussian03.⁶⁸ This method consists of two different functionals: the Becke-3 parameter hybrid exchange functional⁶⁹ and the Perdew 86 correlation functional.⁷⁰ Both potentials use nonlocal exchange-correlation corrections to the density. The current method has shown to reproduce experimental geometries in which there are weak coordinative bonds similar to those in the organometallic compounds studied here.⁷¹ The electronic configurations of the atoms were described by a double- ζ basis set on all atoms. The basis set was augmented with a double-polarization function for all atoms but the metal atom, in which a single $(n + 1)p$ polarization function was added.^{72,73} The core electrons were treated by the relativistic LANL2 pseudopotential.⁷⁴ The most stable arene conformers were previously searched by scanning N-Nb-X1-C and X2-Zr-X1-C dihedral angles for complexes **I** and **II**, respectively (see Figure 2

for nomenclature). The main difference between the complexes is the relative position of the CH₂B(C₆F₅)₃ moiety with respect to the metal fragment. After that, all conformers were optimized without any constraint. Differences less than 2.0 kcal mol⁻¹ have been found for the different conformers, indicating an easy rotation of the arene fragment. In the present paper, we only show the most stable conformers for both complexes. The atomic orbital contributions and overlap populations were calculated with AOMix software.^{75,76} The analysis of the MO composition in terms of occupied and unoccupied fragment molecular orbitals (OFO and UFO, respectively) and construction of molecular orbital interaction diagrams were performed with the AOMix-CDA package.⁷⁷

Polymerization of MMA. The catalyst (4.8×10^{-5} mol) and activator E(C₆F₅)₃ (E = B, Al; 9.6×10^{-5} mol) were handled in the glovebox and introduced into an ampule. The temperature desired was adjusted, and a solution of MMA (9.35 mmol) in 3 mL of toluene was added using Schlenk-vacuum-line techniques. 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 ¹H NMR (CDCl₃) study of the polymer was carried out 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).

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Supporting Information Available: A CIF file giving crystal data for **3b** and figures giving relevant frontier molecular orbitals for the fragment **Ia**, significant molecular orbitals for complexes **I** and **II**, and selected NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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