Polymerization Catalysts

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# Isoprene Polymerization with Yttrium Amidinate Catalysts: Switching the Regio- and Stereoselectivity by Addition of $AlMe_3$**

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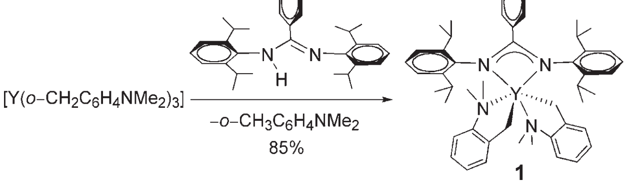
The preparation of polymers with desired microstructures and properties by controlling the regio- and stereoselectivity of olefin polymerization is an important research area. Approaches toward this goal have, to date, mainly involved modifying the ancillary ligands of metal catalysts. The use of chelating amidinate ligands as an alternative to cyclopentadienyl ligands in the development of rare-earth-metal (Group 3 and lanthanide) based polymerization catalysts has received considerable attention.[1,2] Although the majority of amidinate-containing rare-earth-metal complexes reported to date contain two or three amidinate ligands, recent work by Hessen and co-workers has demonstrated that benzamidinates with bulky substituents at the nitrogen atoms, such as *N,N'*-bis(2,6-diisopropylphenyl)benzamidinate $[PhC(NC_6H_4iPr_2\text{-}2,6)_2]^-$, can serve as excellent ancillary ligands for a series of mono(amidinate)/dialkyl or cationic mono(amidinate)/alkyl rare-earth-metal complexes.[2d,e] However, despite the extensive interest in using amidinate rare-earth-metal complexes as polymerization catalysts, the polymerization chemistry reported to date for these complexes has been limited mainly to that of ethylene and polar monomers; studies on the polymerization of higher olefins remain scarce.[1,2] In particular, the use of an amidinate-ligated rare-earth-metal catalyst for the polymerization of a conjugated diene, such as isoprene, has not been reported to date.

We recently found that cationic rare-earth alkyl complexes can serve as excellent catalysts for the polymerization and copolymerization of various olefins.[3,4] During these studies, we became interested in the polymerization of isoprene by cationic rare-earth alkyl complexes bearing a single amidinate ligand, and report herein that the amidinate-ligated yttrium complex $[(NCN^{dipp})Y(o\text{-}CH_2C_6H_4NMe_2)_2]$ (**1**; $NCN^{dipp} = PhC(NC_6H_4iPr_2\text{-}2,6)_2$) is a unique catalyst precursor for the polymerization of isoprene. Thus, complex **1** shows extremely high activity and excellent 3,4-isospecificity for the polymerization of isoprene in the presence of one equivalent of $[Ph_3C][B(C_6F_5)_4]$. More remarkably, however, the regio- and stereoselectivity of this catalyst system can be switched from 3,4-isospecific to 1,4-*cis* selective simply by adding an alkylaluminum compound, such as $AlMe_3$. Although the polymerization of isoprene by various catalyst systems has been studied extensively,[4d,f,5] such a dramatic switching of the regio- and stereoselectivity is, to our knowledge, unprecedented.[6] Isolation of the heterotrinuclear Y/Al complex $[(NCN^{dipp})Y\{(\mu\text{-}Me)_2AlMe_2\}_2]$ (**2**) from the reaction of **1** with $AlMe_3$ and its performance in the polymerization of isoprene are also described.

Treatment of the tris(aminobenzyl)yttrium complex $[Y(o\text{-}CH_2C_6H_4NMe_2)_3]$[7] with one equivalent of the amidine ligand *N,N'*-bis(2,6-diisopropylphenyl)benzamidine ($NCN^{dipp}H$)[8] in THF or toluene at room temperature overnight affords the corresponding mono(amidinate) bis(aminobenzyl) complex **1** in 85 % yield (Scheme 1). The reaction can be completed in 3 h if it is carried out at 70 °C. Complex **1** was fully characterized by $^1H$ and $^{13}C$ NMR spectroscopy, elemental analysis, and X-ray crystallography (Figure 1).[9] The $NCN^{dipp}$ unit in **1** is bonded to the Y center through its two N atoms, as observed in other amidinate complexes.[2] The two aminobenzyl groups are bonded to the Y atom in a chelating fashion through both the N atom and the benzyl carbon atom. Intramolecular coordination of the amino group means that complex **1** does not possess a THF co-ligand, in contrast with the THF-containing $CH_2SiMe_3$ analogue $[(NCN^{dipp})Y(CH_2SiMe_3)_2(thf)]$.[2d] Complex **1** is slightly soluble in hexane but highly soluble in toluene and THF.

The neutral complex **1** does not catalyze the polymerization of isoprene but it becomes extremely active in the presence of one equivalent of $[Ph_3C][B(C_6F_5)_4]$, whereby it converts 750 equivalents of isoprene quantitatively into polyisoprene in 2 min at room temperature. This reaction proceeds with high 3,4-regioselectivity (91 %) and some degree of isotacticity ($mm \approx 50\,\%$) (Table 1, entry 3).[10] When the polymerization is carried out at low temperature ($\leq -10\,°C$), an even higher regio- and stereoselectivity is



**Scheme 1.** Synthesis of the amidinate-ligated bis(aminobenzyl)yttrium complex.

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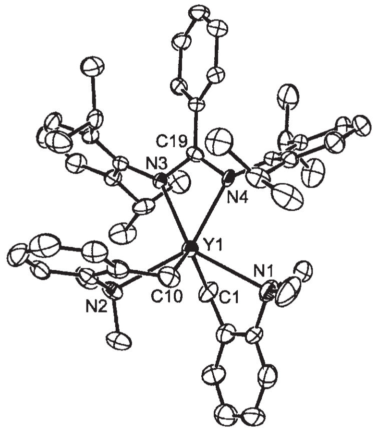
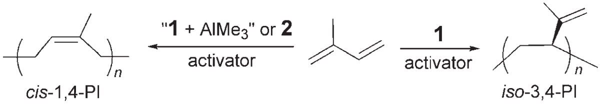


***Figure 1.*** ORTEP structure of **1** (thermal ellipsoids set at 30% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–N1 2.577(3), Y1–N2 2.610(4), Y1–N3 2.369(3), Y1–N4 2.377(3), Y1–C1 2.439(4), Y1–C10 2.413(4); C1-Y1-C10 128.29(14), N3-Y1-N4 55.62(10), N3-C19-N4 111.1(3).

***Table 1:*** Polymerization of isoprene by amidinate-ligated yttrium catalysts.[a]



| Entry | Complex | $AlR_3$ (equiv)[a] | $T_p$ [°C] | $t$ [min] | Yield [%] | $M_n$[b] ($\times 10^4$) | $M_w/M_n$[b] | 3,4/1,4-*cis*/1,4-*trans*[c] | $T_g$[d] [°C] |
|---|---|---|---|---|---|---|---|---|---|
| 1[e] | **1** or **2** | – | 25 | 120 | 0 | – | – | – | – |
| 2 | – | – | 25 | 120 | 80 | 0.3 | 7.9 | 5/15/80 | – |
| 3 | **1** | – | 25 | 2 | 100 | 13.7 | 1.3 | 91/9/0 | 23 |
| 4 | **1** | – | –10 | 20 | 100 | 18.3 | 1.3 | 99/1/0 | 24 |
| 5 | **1** | – | –20 | 20 | 100 | 16.5 | 1.4 | 99.5[f]/0.5/0 | 22[g] |
| 6 | **1** | Al*i*Bu$_3$ (5) | 25 | 10 | 100 | 9.9 | 1.3 | 96/3.9/0.1 | 21 |
| 7 | **1** | AlEt$_3$ (5) | 25 | 10 | 100 | 6.1 | 1.2 | 96/4/0 | 22 |
| 8 | **1** | AlMe$_3$ (5) | 25 | 10 | 100 | 6.6 | 1.6 | 3/91/6 | –63 |
| 9 | **1** | AlMe$_3$ (10) | 25 | 10 | 100 | 6.3 | 1.5 | 3/91/6 | –63 |
| 10 | **1** | AlMe$_3$ (4) | 25 | 10 | 100 | 7.0 | 1.6 | 4/90/6 | –59 |
| 11 | **1** | AlMe$_3$ (3) | 25 | 10 | 100 | 7.1 | 1.5 | 9/90/1 | –59 |
| 12 | **1** | AlMe$_3$ (2) | 25 | 10 | 100 | 9.2 | 1.5 | 86/14/0 | 21 |
| 13 | **1** | AlMe$_3$ (5) | –10 | 60 | 82 | 17.6 | 1.6 | 1/98/1 | –66 |
| 14 | **1** | AlMe$_3$ (5) | –20 | 960 | 100 | 40.1 | 1.7 | 1/>98/<1 | –67 |
| 15[e] | **1** | AlMe$_3$ (5) | 25 | 120 | 0 | – | – | – | – |
| 16 | – | AlMe$_3$ (5) | 25 | 120 | 60 | 0.8 | 4.7 | 7/8/85 | – |
| 17 | **2** | – | 25 | 10 | 100 | 6.8 | 1.8 | 22/77.8/0.2 | –57 |
| 18 | **2** | AlMe$_3$ (1) | 25 | 10 | 100 | 7.5 | 1.6 | 6/92/2 | –59 |

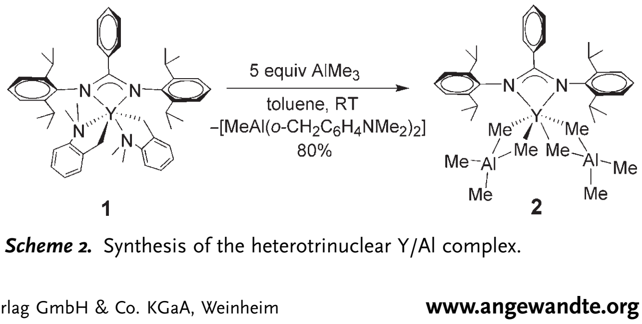
[a] Conditions: $C_6H_5Cl$ (10 mL); **1** or **2** (Y, 20 μmol); isoprene (1.022 g); $[Y]_0/[Ph_3C][B(C_6F_5)_4]_0 = 1{:}1$, equiv $= [AlR_3]_0/[Y]_0$, unless otherwise noted. [b] Determined by GPC with respect to a polystyrene standard. [c] Determined by $^1H$ and $^{13}C$ NMR spectroscopy. [d] Determined by DSC. [e] Without $[Ph_3C][B(C_6F_5)_4]$. [f] *mm* = 100%, *mmmm* = 99%. [g] $T_m = 142\,°C$ was also observed.

achieved and almost perfectly isotactic 3,4-polyisoprene is obtained (3,4-selectivity up to 99.5%, *mmmm* up to 99%; Table 1, entries 4 and 5).

In a subsequent reaction $AlR_3$ (R = *i*Bu, Et, Me) was added to the catalyst system to see whether alkylaluminum compounds have any influence on the polymerization. The addition of Al*i*Bu$_3$ or AlEt$_3$ had little effect on the polymerization (Table 1, entries 6 and 7, respectively).[11] To our surprise, however, addition of $AlMe_3$ ($[AlMe_3]_0/[\mathbf{1}]_0 \geq 3$) to the **1**/$[Ph_3C][B(C_6F_5)_4]$ system changed the regio- and stereoselectivity of the polymerization dramatically from 3,4-isospecific to 1,4-*cis* selective (Table 1, entries 8–11). In the presence of five equivalents of $AlMe_3$ at –10 °C or below, the 1,4-*cis* selectivity is as high as 98% and the reaction produces 1,4-*cis*-polyisoprene with an $M_n$ of up to $4.01 \times 10^5$ and an $M_w/M_n$ ratio of around 1.7 (Table 1, entries 13 and 14). The polymerization system remains 3,4-selective in the presence of two or fewer equivalents of $AlMe_3$ (Table 1, entries 12). For comparison, the combination **1**/$AlMe_3$ does not show catalytic activity for isoprene polymerization in the absence of $[Ph_3C][B(C_6F_5)_4]$ (Table 1, entries 15), while the combination $AlMe_3/[Ph_3C][B(C_6F_5)_4]$ yields polyisoprene containing 1,4-*trans* units as the main component (Table 1, entry 16).

To gain a better understanding of the effect of $AlMe_3$ observed in the above polymerizations, the reaction of **1** with $AlMe_3$ was examined further. Thus, complex **1** reacts rapidly with five equivalents of $AlMe_3$ in toluene at room temperature to give the heterotrinuclear Y/Al complex **2** in 80% yield (Scheme 2).[12] As shown by an X-ray diffraction study, complex **2** can formally be viewed as a combination of one molecule of $[(NCN^{dipp})YMe_2]$ with two molecules of $AlMe_3$ (Figure 2).[9] The Y atom and each of the two Al atoms in this complex are bridged by two Me groups, and a crystallographic twofold axis passes through the Y atom and the central carbon atom of the $NCN^{dipp}$ amidinate unit. The eight methyl groups in **2** exhibit only one singlet at around $\delta = 0.02$ ppm in the $^1H$ NMR spectrum in $[D_8]$toluene at both room temperature and –60 °C, thereby suggesting a rapid exchange between the bridging and terminal methyl groups in solution.[13]

Complex **2** alone is not an active isoprene polymerization catalyst. However, in the presence of one equivalent of $[Ph_3C][B(C_6F_5)_4]$ at room temperature it rapidly produces polyisoprene with around 78% 1,4-*cis* selectivity (Table 1, entry 17), which contrasts with the 3,4-selectivity of the aluminum-free



***Scheme 2.*** Synthesis of the heterotrinuclear Y/Al complex.

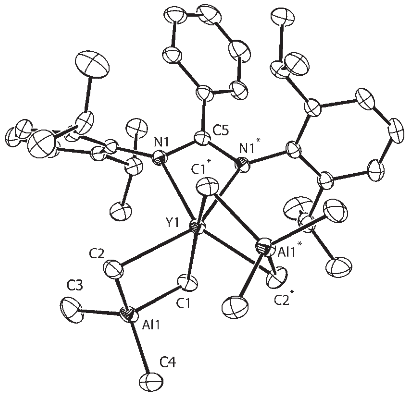
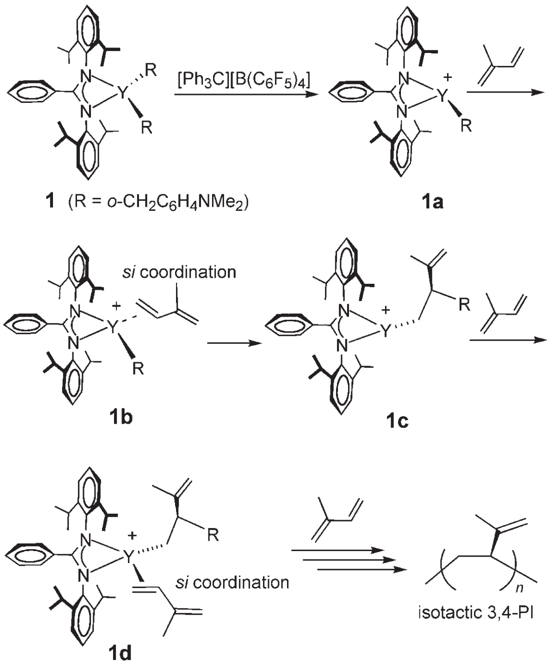


***Figure 2.*** ORTEP structure of **2** (thermal ellipsoids set at 30% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–N1 2.3157(15), Y1–C1 2.542(2), Y1–C2 2.523(2), Al1–C1 2.071(2), Al1–C2 2.041(3), Al1–C3 1.963(2), Al1–C4 1.967(2); C1-Y1-C2 81.94(8), C1-Y1-C1* 165.04(10), C1-Y1-C2* 89.71(8), C1-Y1-N1 96.02(6), C1-Y1-N1* 97.09(6), C2-Y1-C1* 89.71(8), C2-Y1-C2* 112.18(11), C2-Y1-N1 95.20(7), C2-Y1-N1* 152.57(7), N1-Y1-N1* 57.51(8), N1-C5-N1* 112.0(2).

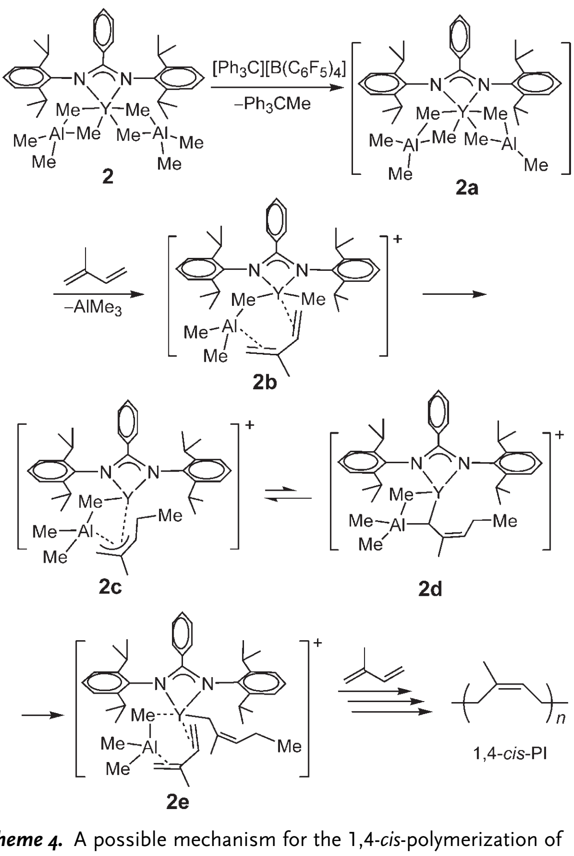
system **1**/[$Ph_3C$][$B(C_6F_5)_4$] (Table 1, entry 3). Addition of one equivalent of $AlMe_3$ to the **2**/[$Ph_3C$][$B(C_6F_5)_4$] system further raises the 1,4-*cis* selectivity to 92% (Table 1, entry 18), which is close to that (ca. 91% 1,4-*cis* selectivity) obtained in the **1**/[$Ph_3C$][$B(C_6F_5)_4$]/$AlMe_3$ ($[AlMe_3]_0/[\mathbf{1}]_0 \geq 3$) three-component systems (Table 1, entries 8–11). These results suggest that the active species for the 1,4-*cis* polymerization of isoprene in the present catalyst systems is likely to be a cationic Y/Al heteronuclear species.

A possible mechanism for the isospecific 3,4-polymerization of isoprene by **1**/[$Ph_3C$][$B(C_6F_5)_4$] can be proposed on the basis of the results observed above and those reported previously (Scheme 3).[2d,e,4h] Thus, the reaction of **1** with [$Ph_3C$][$B(C_6F_5)_4$] gives a cationic aminobenzyl species such as **1a**.[2d,e,4h,14] The steric hindrance and $C_2$ symmetry of the $(NCN^{dipp})$Y unit means that coordination of isoprene to the Y center in **1a** takes place preferably in a 3,4-$\eta^2$ fashion through the *si* face to give **1b**.[4d,15] Subsequent migratory addition of the aminobenzyl group to the coordinated isoprene in **1b** affords **1c**, followed by multiple subsequent 3,4-coordination and isoprene insertion steps, leads to the formation of isotactic 3,4-polyisoprene.

The reaction of **1**/$AlMe_3$ or **2** with [$Ph_3C$][$B(C_6F_5)_4$] probably first yields a cationic, heterotrinuclear Y/Al species, such as **2a** (Scheme 4).[12,16] The coordination of isoprene probably takes place at a heterobimetallic Y/Al unit in a μ-*cis*-1,4-$\eta^4$ fashion by replacement of an $AlMe_3$ unit in **2a** to give **2b**. The 1,4-addition of a methyl group to the coordinated isoprene gives a μ-π-*anti*-allyl species, such as **2c**, which could be in an equilibrium with the μ-σ-allyl species **2d**. Subsequent repeated isoprene coordination and insertion would yield 1,4-*cis*-polyisoprene.



***Scheme 3.*** A possible mechanism for the isospecific 3,4-polymerization of isoprene by **1**/[$Ph_3C$][$B(C_6F_5)_4$].



***Scheme 4.*** A possible mechanism for the 1,4-*cis*-polymerization of isoprene by **2**/[$Ph_3C$][$B(C_6F_5)_4$] or **1**/[$Ph_3C$][$B(C_6F_5)_4$]/$AlMe_3$.

In summary, we have demonstrated that an amidinate-ligated aminobenzylyttrium complex such as **1**, in combination with [$Ph_3C$][$B(C_6F_5)_4$], is an excellent catalyst system for the isospecific 3,4-polymerization of isoprene. More remarkably, the regio- and stereoselectivity of this polymerization system can be dramatically switched from 3,4-isospecific to 1,4-*cis* selective by addition of $AlMe_3$. Isolation of the heterotrinuclear Y/Al complex **2** from the reaction of **1** with $AlMe_3$, and the 1,4-*cis* specificity of the **2**/[$Ph_3C$][$B(C_6F_5)_4$] system for the polymerization of isoprene, suggests that this selectivity switching from 3,4-isospecific to 1,4-*cis* selective could be due to the involvement of a cationic, heterobimetallic Y/Al catalyst species. Although alkylaluminum compounds have often been used as additives or cocatalysts in various isoprene polymerization catalyst systems, this is the first report to unambiguously show that the incorporation of an alkylaluminum species can dramatically change the regio- and stereoselectivity of a catalyst system.

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[6] Switching the selectivity of isoprene polymerization from 1,4-*cis* (75%) to 1,4-*trans* (90%) by replacing the MAO activator with $AlEt_3$ or $Al\textit{i}Bu_3$ in an yttrium-based catalyst system has been reported previously.[5j] A similar reaction was also observed for butadiene polymerization: R. Taube, H. Windisch, S. Maiwald, H. Hemling, H. Schumann, *J. Organomet. Chem.* **1996**, *513*, 49–61.

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[9] CCDC-657217 (**1**) and CCDC-657218 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] The use of the THF-containing $CH_2SiMe_3$ analogue $[(NCN^{dipp})Y(CH_2SiMe_3)_2(thf)]$ instead of **1** gave a similar result in terms of selectivity but with a lower activity. The polymerization in toluene also showed a similar selectivity, although the activity was somewhat lower than that in chlorobenzene because of lower solubility.

[11] The molecular weight of the resulting polymers decreased when $AlR_3$ was added, probably a result of chain transfer to the aluminum atom.

[12] The reaction of **1** with $Al\textit{i}Bu_3$ or $AlEt_3$ was much slower than that with $AlMe_3$. This could be a reason why $Al\textit{i}Bu_3$ or $AlEt_3$ have little effect on the polymerization selectivity.

[13] For similar complexes, see: a) R. Anwander, M. G. Klimpel, H. M. Dietrich, D. J. Shorokhov, W. Scherer, *Chem. Commun.* **2003**, 1008–1009; b) H. M. Dietrich, C. Zapilko, E. Herdtweck, R. Anwander, *Organometallics* **2005**, *24*, 5767–5771.

[14] Formation of the cationic species $[(NCN^{dipp})Y(\text{-}o\text{-}CH_2C_6H_4NMe_2)(thf)_x][B(C_6F_5)_4]$ was confirmed by $^1H$ NMR spectroscopy in $[D_8]THF$: $\delta = 7.18$–$6.59$ (m, 15H; aromatic), 3.33 (m, 4H; $\text{-}C\textit{H}Me_2$), 2.51 (s, 6H; $\text{-}o\text{-}CH_2C_6H_4N\textit{Me}_2$), 2.07 (s, 2H; $\text{-}o\text{-}C\textit{H}_2C_6H_4NMe_2$), 1.30 (d, $J = 3$ Hz, 3H; $\text{-}CH\textit{Me}_2$), 0.80 ppm (d, $J = 3$ Hz, 3H; $\text{-}CH\textit{Me}_2$). The THF-free analogue is unstable.

[15] Computational studies suggest that only the 3,4-coordination of isoprene to the metal center in **1a** is permitted as the 1,4-coordination mode (either *cis* or *trans*) is not accessible. See the Supporting Information for details.

[16] Attempts to isolate a cationic heterobimetallic Y/Al species from either the reaction of **2** with $[Ph_3C][B(C_6F_5)_4]$ or the reaction of **1**/$[Ph_3C][B(C_6F_5)_4]$ with $AlMe_3$ have not yet been successful because of its instability.