Synthesis and Structure of a Four-Coordinate Aluminum Alkyl Cation/$HB(C_6F_5)_3$ Salt: Implication in a $B(C_6F_5)_3$-Catalyzed Hydroalumination Reaction of Benzophenone or Benzaldehyde

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The reaction of the bulky aminophenol 2-(CH_2NMe_2)-4-Me-6-CPh_3-C_6H_3OH (**1**) with Al(^{i}Bu)$_3$ yields via isobutane elimination the formation of the diisobutyl Al complex {6-(CH_2-NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(^{i}Bu)$_2$ (**2**) in high yield. Reaction of **2** with $B(C_6F_5)_3$ in the presence of NMe_2Ph affords, along with isobutene, the salt compound [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(^{i}Bu)(NMe_2Ph)][$HB(C_6F_5)_3$] (**3**), consisting of a four-coordinate Lewis acidic Al cation associated with the borohydride $HB(C_6F_5)_3^-$, whose solid-state structure was determined by X-ray crystallography. When complex **2** is reacted with $B(C_6F_5)_3$ (1 and 0.05 equiv) in the presence of benzophenone and benzaldehyde, the quantitative conversion to the hydroalumination products **4** and **5**, respectively, is observed. This $B(C_6F_5)_3$-catalyzed hydroalumination reaction, via a $B(C_6F_5)_3$-mediated hydride abstraction/transfer reaction, represents a new type of reactivity for Al alkyl cations and illustrates the higher reactivity of Al cation/$HB(C_6F_5)_3^-$ salts versus the classical Al cation/$MeB(C_6F_5)_3^-$ and $B(C_6F_5)_4^-$ salts.

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Introduction

Low-coordinate cationic Al species have recently received increased attention because the potent Lewis acid character of the obtained Al cations, a result of the cationic charge at the Al center, is of potential interest for Lewis acid catalysis.[1] In this regard, cationic alkyl Al species of the type {LX}$AlMe^+$ are particularly interesting targets, since they can be readily accessible from {LX}$AlMe_2$ via a Me^- abstraction by strong Lewis acids such as $B(C_6F_5)_3$ at the Al center.[2] Several studies have shown that the stability of these cationic species is strongly dependent on the inertness of the counterion and on the presence of a Lewis base L in the medium to stabilize the Al cation by forming {LX}Al(Me)$(L)^+$ adducts.[3] Thus, the $MeB(C_6F_5)_3^-$ and $B(C_6F_5)_4^-$ anions, which are among the least reactive anions known so far, are typically associated with low-coordinate Al cations, yielding, in most cases, stable {LX}Al(Me)$(L)^+$ cations.[2,3]

Alternatively, although synthetically challenging, the use of more reactive and more Lewis basic counterions for association with a Lewis acidic Al cation appears interesting, since the resulting salt compound would include both a Lewis acidic and basic entity. This complementarity may be useful for the functionalization of some unsaturated substrates: i.e., (i) activation of the substrate by coordination to the Al cation followed by (ii) reaction of the Lewis basic anion with the coordinated substrate.

We reported earlier that the reactions of monoaminophenolate-*N*,*O* dialkyl Al complexes {2-(CH_2NMe_2)-6-R-C_6H_3O}$AlMe_2$ (R = ^{t}Bu, Ph) with $B(C_6F_5)_3$ lead to stable dinuclear cationic Al species as $MeB(C_6F_5)_3^-$ salts, whose reactivity was then studied.[4] To prevent such aggregation and thus to favor the obtainment of mononuclear cationic species, we became interested in the synthesis of Al alkyl cations incorporating a more bulky bidentate aminophenolate. The CPh_3 ortho-substituted aminophenolate ligand A (Chart 1) seemed a good candidate for this purpose, because the significant steric crowding around the Al center should promote the formation and the stability of mononuclear Al species. As part of our studies on the reactivity of {2-(CH_2NMe_2)-4-Me-6-CPh_3-C_6H_3O}AlR_2 with $B(C_6F_5)_3$, we here report that the ionization reaction of {2-(CH_2-NMe_2)-4-Me-6-CPh_3-C_6H_3O}Al^iBu_2 with $B(C_6F_5)_3$ in the

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(1) Atwood, D. A. *Coord. Chem. Rev.* **1998**, *176*, 407.

(2) For leading references, see: (a) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125. (b) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 2523. (c) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673.

(3) (a) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274. (b) Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 8291.

(4) Dagorne, S.; Lavanant, L.; Welter, R.; Chassenieux, C.; Haquette, P.; Jaouen, G. *Organometallics* **2003**, *22*, 3732.

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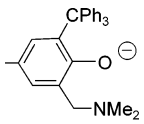
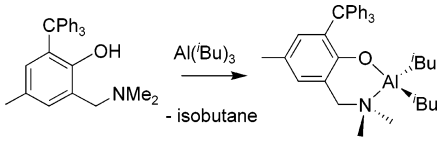
Chart 1



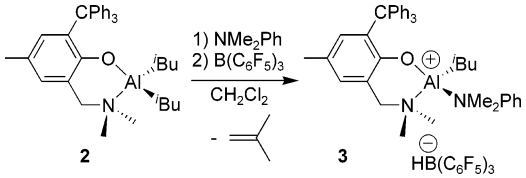
A

Scheme 1



1 2

Scheme 2



2 3

presence of an appropriate Lewis base L affords an unprecedented salt compound, associating a Lewis acidic Al−L cation with the $HB(C_6F_5)_3^-$ anion, a hydride source. The potential reactivity of this salt is illustrated here by its implication in the $B(C_6F_5)_3$-catalyzed hydroalumination of benzophenone or benzaldehyde, which involves the reduction of a carbonyl group by $HB(C_6F_5)_3^-$.

Results and Discussion

The reaction of the aminophenol 2-(CH_2NMe_2)-4-Me-6-CPh_3-C_6H_3OH (**1**; Scheme 1), synthesized according to known literature procedures,[5] with 1 equiv of Al(^{i}Bu)$_3$ at −40 °C in pentane affords, along with isobutane evolution, the corresponding Al diisobutyl complex {6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(^{i}Bu)$_2$ (**2**; Scheme 1) in high yield as an analytically pure colorless solid. The NMR data for complex **2** at room temperature in C_6D_6 are consistent with the chelation of one aminophenolate ligand to the Al center. Under the studied conditions, the NMR data for **2** show an effective C_s symmetry, which may be ascribed to a fast conformation change of the six-membered-ring Al metallacycle on the NMR time scale, as previously observed for related monoaminophenolate group 13 complexes.[6] For example, the ^{1}H NMR spectrum of the diisobutyl Al complex **2** exhibits two CH_3 ^{i}Bu resonances (δ 0.69, 0.64) and two CH_2 ^{i}Bu resonances (δ −0.39, −0.45) but contains only one CH ^{i}Bu signal (δ 1.48), as expected for the proposed symmetry.

The NMR-scale reaction of the diisobutyl Al complex **2** with 1 equiv of $B(C_6F_5)_3$ (CD_2Cl_2, 15 min, room temperature) in the presence of 1 equiv of NMe_2Ph yields the quantitative formation of the four-coordinate cationic Al−NMe_2Ph adduct as a $HB(C_6F_5)_3^-$ salt, [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(^{i}Bu)(NMe_2Ph)][HB(C_6F_5)$_3$] (**3**, Scheme 2), along with isobutene formation, as observed by ^{1}H NMR. This reaction most likely proceeds via a hydride abstraction reaction at C_β of one Al−^{i}Bu moiety of complex **2**, as evidenced by the presence of isobutene and of the $HB(C_6F_5)_3^-$ anion.[7] As anticipated, compound **3** is less stable than related [{LX}Al(Me)(NMe_2Ph)][$MeB(C_6F_5)_3$] salt compounds and slowly decomposes over 2−3 days in CD_2Cl_2 at room temperature to yield unknown products. The preparative-scale generation of salt compound **3** allowed its obtainment as a colorless solid, although not analytically pure (see Experimental Section).

Attempts to perform similar ionization reactions using less bulky aminophenolate Al−diisobutyl complexes {2-(CH_2NMe_2)-6-R-C_6H_3O}Al^{i}Bu$_2$ (R = ^{t}Bu, Ph)[8] only allowed the fleeting observation of the desired species [{2-(CH_2NMe_2)-6-R-C_6H_3O}Al(^{i}Bu)(NMe_2Ph)][$HB(C_6F_5)_3$], followed by fast decomposition to unknown species. These observations strongly suggest that a significant steric crowding at the Al center is a key requirement to obtain stable [{LX}Al(^{i}Bu)(L)][$HB(C_6F_5)_3$]. In addition, the nature of the L Lewis base coordinated to the cationic Al center also appears to be critical for the stability of these salt compounds. Thus, when the Al diisobutyl complex **2** is reacted with $B(C_6F_5)_3$ in the presence of THF, an intractable mixture of products is obtained, which contrasts with the general straightforward generation and good stability of [{LX}Al(Me)(THF)][$MeB(C_6F_5)_3$] salts. Overall, changing from $MeB(C_6F_5)^{3-}$ to the more Lewis basic $HB(C_6F_5)_3^-$ anion, a formal hydride source, dramatically decreases the stability of the formed salts.

Solution and Solid-State Structures of the Salt Compound 3. The ^{1}H, ^{11}B, and ^{19}F NMR data for **3** in C_6D_6 at room temperature are consistent with the presence of the $HB(C_6F_5)_3^-$ anion and with this anion being free in solution under these conditions, as its NMR data closely matched those for the ammonium salt [Bu_4N][$HB(C_6F_5)_3$].[9] For example, the ^{1}H NMR spectrum of **3** contains a broad doublet (δ 4.15) assigned to the HB hydride, whereas the ^{11}B NMR spectrum exhibits a doublet (δ −25.7), which is in agreement with a BH-type four-coordinate borate.[9] The NMR data for the Al−NMe_2Ph cation at room temperature clearly evidence the coordination of the aniline to the cationic Al center and show an effective overall C_1 symmetry for the Al cation, as a result of the coordination of the aniline to the Al center. In particular, the ^{1}H and ^{13}C NMR spectra of **4** both display two resonances for the Me groups of the coordinated NMe_2Ph as well as two signals for the N*Me*$_2$ group of the aminophenolate ligand.

The solid-state structure of complex **3** was determined by X-ray crystallographic analysis. The molecular structure of **3** and selected bond distances and angles are shown respectively in Figure 1 and Table 2, and crystallographic data are given in Table 1. The salt compound **3** crystallizes as {6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(^{i}Bu)(NMe_2Ph)$^+$ and $HB(C_6F_5)_3^-$ ions with no close cation−anion interactions. Each asymmetric unit contains two independent molecules of **3**, and both of

(5) Tramontini, M. *Synthesis* **1973**, 103.

(6) Hagen, H.; Reinoso, S.; Albrecht, M.; Boersma, J.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **2000**, *608*, 27. See also ref 4.

(7) [Ph_3C][$B(C_6F_5)_4$] was also reported to β-abstract an hydride at neutral {LX}Al(^{i}Bu)$_2$Al complexes to yield Ph_3CH, isobutene, and an Al−^{i}Bu$^+$ cation. For more details, see: Ihara, E.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 8277.

(8) Dagorne, S.; Jaouen, G. Unpublished results.

(9) Blackwell, J. M.; Morrison, D. J.; Piers, W. E. *Tetrahedron* **2002**, *58*, 8247.

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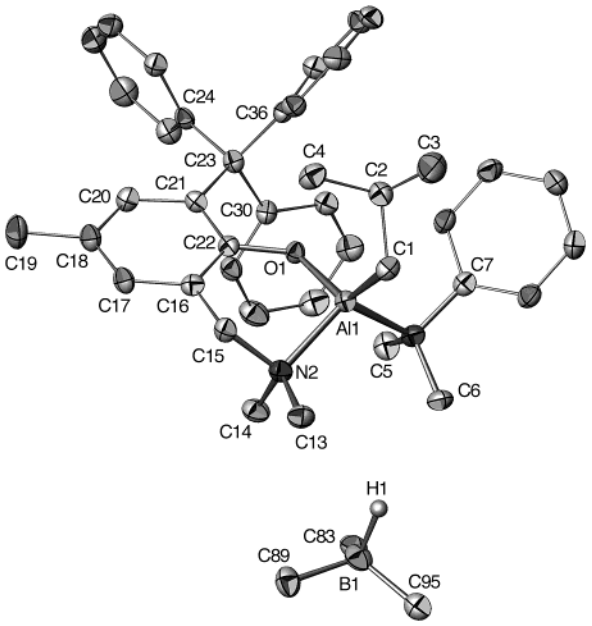


Figure 1. Molecular structure of the salt compound **3**. The H atoms (except B*H*) and the C_6F_5 groups of the $HB(C_6F_5)_3^-$ anion are omitted for clarity. Some atoms of the Al cation are not labeled for the same reason. Selected torsion angles (deg): |Al(1)−O(1)−C(22)−C(16)| = 3.3(1), |Al(1)−O(1)−C(16)−C(15)| = 1.8(1), |O(1)−Al(1)−N(2)−C(15)| = 53.5(2), |O(1)−C(22)−C(15)−N(2)| = 35.8(1).

Table 1. Crystal Data and Structure Refinement Details for 3

formula	$C_{41}H_{48}AlN_2OHBC_{18}F_{15}$
formula wt	1124.79
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a (Å)	11.4160(10)
b (Å)	21.473(3)
c (Å)	24.265(3)
α (deg)	68.61(5)
β (deg)	77.52(5)
γ (deg)	81.59(5)
V (Å^3)	5392.9(11)
Z	4
calcd density (g cm^{-3})	1.385
μ(Mo Kα) (mm^{-1})	0.133
F(000)	2312
cryst color	colorless
cryst size (mm)	0.13 × 0.10 × 0.08
temp (K)	173
min, max *θ* (deg)	1.59, 27.85
data set (*h*; *k*; *l*)	−14 to +14; −25 to +28; 0−31
total and unique no. of data; *R*(int)	25 464, 25 463; 0.026
no. of obsd data ($I > 2\sigma(I)$)	18 101
N_{rfln}, N_{param}	25 463, 1431
R1, wR2, GOF[a]	0.0904, 0.2485, 0.895
max, av shift/error	0.001, 0.00
min, max desd. dens (e Å^{-3})	−0.469, 1.123

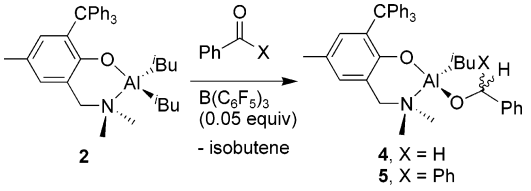
[a] $w = 1/[\sigma^2(F_o^2) + (0.1749P)^2 + 2.2774P]$; $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Cation in 3

Al(1)−O(1)	1.735(3)	Al(1)−N(2)	1.985(4)
Al(1)−N(1)	1.991(4)	Al(1)−C(1)	1.946(4)
O(1)−Al(1)−N(2)	97.8 (1)	O(1)−Al(1)−N(1)	104.9(1)
O(1)−Al(1)−C(1)	122.2(2)	N(2)−Al(1)−N(1)	109.7(1)

them exhibit structural features nearly identical with one another. The $HB(C_6F_5)_3^-$ anion, shown in Figure 1 without the C_6F_5 rings for clarity, has a normal structure, in which the boron adopts a nearly ideal tetrahedral geometry. The Al cation is an aniline-stabilized four-coordinate Al species, in which the Al center adopts a slightly distorted tetrahedral structure with a N−Al−O chelate bite angle (98.0(2)° average). The six-membered-ring chelate Al metallacycle is significantly twisted, with the NMe_2 group above the nearly planar $OAlC_3$ backbone, as shown by the torsion angle values of |Al(1)−O(1)−C(22)−C(16)| and |Al(1)−O(1)−C(16)−C(15)| (3.3 and 1.8°, respectively) versus those of |O(1)−Al(1)−N(2)−C(15)| and |O(1)−C(22)−C(15)−N(2)| (53.5 and 35.8°, respectively). The Al−O and Al−N bond distances of the chelated aminophenolate (1.735(6) and 1.99(1) Å, respectively) are slightly shorter than those in the related neutral Al dimethyl complex {6-(CH_2NMe_2)-2-^{t}Bu-C_6H_2O}$AlMe_2$ (1.758(1) and 2.036(5) Å, respectively),[4] as expected from the more electrophilic cationic Al center in **2** vs that in a neutral derivative. The Al−$N_{aniline}$ bond distance (1.99(1) Å) is normal for a Al−N dative bond and is comparable with that in the dinuclear Al cation (^{t}BuMe_2SiO)$_2Al_2Me_3(NMe_2Ph)^+$, which also contains an aniline-stabilized four-coordinate Al cationic center. Overall, the solid-state structure of **3** clearly shows the significant steric bulk around the Al center, which, in part, justifies the relatively good stability of this salt.

Scheme 3



B(C_6F_5)$_3$-Catalyzed Hydroalumination of Ph_2CO and PhCHO in the Presence of Complex 2. To probe the reactivity of Al cation/$HB(C_6F_5)_3^-$ salt compounds as a Lewis acid and base system, carbonyl substrates seemed appropriate, since they may act as Lewis bases toward the formed Al cation while being susceptible to hydride attack from $HB(C_6F_5)_3^-$.

The diisobutyl Al complex **2** cleanly reacts with 1 equiv of $B(C_6F_5)_3$ in the presence of 1 equiv of benzophenone and benzaldehyde (CD_2Cl_2, 15 min, room temperature) to quantitatively afford the corresponding neutral monoalkoxy monoisobutyl complexes {6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(O−C(H)(R)Ph)(^{i}Bu) (**4**, R = H; **5**, R = Ph; Scheme 3), along with the evolution of isobutene, as observed by ^{1}H NMR on a NMR-scale reaction. The ^{19}F NMR data of the reaction mixture only contain signals for 1 equiv of $B(C_6F_5)_3$. When this reaction is performed using 0.05 equiv of $B(C_6F_5)_3$, complete conversion to complexes **4** and **5** (CD_2Cl_2, room temperature, complete conversion to **4** after 3 h and to **5** after 5 h) is also observed by ^{1}H NMR, along with isobutene formation, without consumption of any $B(C_6F_5)_3$, as observed by ^{19}F NMR.[10] Compounds **4** and **5** were generated on a preparative scale in CH_2Cl_2 and isolated in a pure form after evaporation of the volatiles and a subsequent pentane wash (see Experimental Section).

(10) The NMR-scale generation of complexes **4** and **5** was carried out using hexamethylbenzene (0.3 equiv vs **2**) and Li[$B(C_6F_5)_4$] (0.5 equiv vs **2**) as internal standards for ^{1}H and ^{19}F NMR analysis, respectively.

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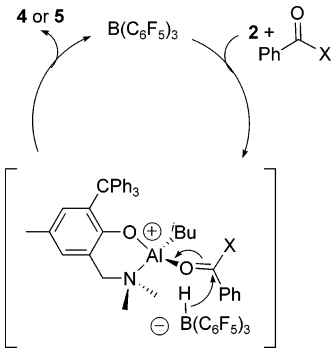
Scheme 4



The NMR data for both complexes agree with the proposed structures and with overall C_1-symmetry structures, as expected. For example, the ^{1}H NMR spectrum of **4** exhibits an AB pattern (δ 4.37) consistent with the benzyl protons of the Al−OCH_2Ph moiety, whereas that of **5** contains a singlet resonance (δ 5.36) characteristic of the Al−$OCHPh_2$ benzylic proton. Thus, these results are consistent with $B(C_6F_5)_3$ catalytically converting the diisobutyl complex **2** to the monoalkoxy complexes **4** and **5** in the presence of the appropriate carbonyl derivative. In contrast, attempts to perform these hydroalumination reactions using enolizable ketones such as acetophenone yielded intractable mixtures of products, in which neither a hydroalumination product nor an enolized product was present.

A possible mechanism for the hydroalumination reaction described here is presented in Scheme 4. The initial reaction of complex **2** with $B(C_6F_5)_3$, in the presence of the carbonyl derivative acting as a Lewis base L, probably leads to the formation of a transient species that can be related to **3**: i.e., the four-coordinate cationic Al−L adduct {6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(^{i}Bu)-$(L)^+$ as a $HB(C_6F_5)_3^-$ salt, along with release of isobutene. The $HB(C_6F_5)_3^-$ borohydride may then transfer back an hydride to the quite electrophilic *C*═O carbon, thus producing complex **4** or **5** and regenerating $B(C_6F_5)_3$. The mechanism proposed here, i.e., a $B(C_6F_5)_3$-mediated hydride abstraction/transfer reaction, is reminiscent of that found in the $B(C_6F_5)_3$-catalyzed hydrosilation of carbonyl functions, studied by Piers and al.[11]

Conclusions

The synthesis and structure of the salt compound [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(^{i}Bu)(NMe_2Ph)][HB-$(C_6F_5)_3$] show that low-coordinate cationic Al species of the type $\{LX\}Al(R)(L)^+$ may be stable in the presence of a borohydride anion such as $HB(C_6F_5)_3^-$, provided there is a significant steric protection of the Al metal center and a Lewis base L not susceptible to hydride attack is used. The increased reactivity of the $HB(C_6F_5)_3^-$ vs the $MeB(C_6F_5)_3^-$ or $B(C_6F_5)_4^-$ salts is illustrated here by a $B(C_6F_5)_3$-catalyzed hydroalumination of Ph_2CO and PhCHO, in which a four-coordinate Al cation/HB-$(C_6F_5)_3^-$ salt is most probably involved. This new type of reactivity for Al alkyl cations may be of interest for other catalytic applications.

Further studies will focus on the use of different unsaturated organic substrates as well as on the use of different Lewis basic anions that could be associated with a Al cation.

Experimental Section

General Procedures. All experiments were carried out under N_2 using standard Schlenk techniques or in an MBraun Unilab glovebox. Toluene, pentane, and diethyl ether were distilled from Na/benzophenone and stored over activated molecular sieves (4 Å) in a glovebox prior to use. CH_2Cl_2 and CD_2Cl_2 were distilled from CaH_2 and stored over activated molecular sieves (4 Å) in a glovebox prior to use. C_6D_6 was degassed under a N_2 flow and stored over activated molecular sieves (4 Å) in a glovebox prior to use. The phenol derivative 2-CPh_3-4-Me-C_6H_3OH was prepared by following a literature procedure.[12] $B(C_6F_5)_3$ was purchased from Strem and extracted with dry pentane prior to use. All other chemicals were purchased from Aldrich and were used as received, except NMe_2Ph, which was stored over activated molecular sieves (4 Å) prior to use. NMR spectra were recorded on Bruker AC 200 and 400 MHz NMR spectrometers, in Teflon-valved J. Young NMR tubes at ambient temperature, unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported vs $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks. ^{11}B and ^{19}F chemical shifts are reported versus $BF_3{\cdot}Et_2O$ in CD_2Cl_2 and neat $CFCl_3$, respectively. Elemental analyses were performed by Mikroanalytisches Labor Pascher (Remagen-Bandorf, Germany), except that for compound **1**, which was carried out by the microanalysis laboratory of the Université Pierre et Marie Curie (Paris, France).

6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2OH (1). The disubstituted phenol 2-CPh_3-4-Me-C_6H_2OH (1.00 g, 2.85 mmol), dimethylamine (2.15 mL of a 40% aqueous solution, 17,1 mmol), and formaldehyde (1.25 mL of a 37% aqueous solution, 17.1 mmol) were added to a 50 mL round-bottom flask and dissolved in 15 mL of ethanol. The reaction mixture was refluxed for 40 h, and upon cooling to room temperature, 6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_3OH precipitated out of solution as a colorless solid. The mixture was filtered and the colorless solid washed with cold ethanol and pentane to afford, after drying under vacuum, pure 6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2OH (900 mg, 78% yield). Anal. Calcd for $C_{29}H_{29}NO$: C, 85.47; H, 7.17; N, 3.44. Found: C, 85.47; H, 7.28; N, 3.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.13 (m, 15H, C*Ph*$_3$), 6.89 (d, ^4J(HH) = 2.0 Hz, 1H, *Ph*−O), 6.78 (d, ^4J(HH) = 2.0 Hz, 1H, *Ph*−O), 3.54 (s, 2H, PhCH_2), 2.21 (s, 3H, *Me*Ph), 2.13 (s, 6H, NMe_2). ^{13}C NMR (100 MHz, $CDCl_3$): d 154.1 (O−*Ph*), 146.0 (Ph), 133.8 (Ph), 131.0 (Ph), 130.5 (Ph), 128.1 (Ph), 126.7 (Ph), 126.4 (Ph), 125.8 (Ph), 122.3 (Ph), 63.1 (*C*Ph_3), 62.6 (Ph*C*H_2), 43.8 (N*Me*$_2$), 20.8 (*Me*Ph).

{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(^{i}Bu)$_2$ (2). In a glovebox, a pentane suspension (6 mL) of the aminophenol **1** (800.0 mg, 1.96 mmol) precooled to −40 °C was slowly added via a pipet to a vial containing a pentane solution (5 mL) of Al(^{i}Bu)$_3$ (389.3 mg, 1.96 mmol). After the addition, the reaction mixture (colorless suspension) was warmed to room temperature with the vial loosely capped to allow isobutane escape and was stirred for 18 h. The resulting suspension was filtered through a glass frit to afford, after drying in vacuo, the diisobutyl Al complex **2** as a colorless solid (912 mg, 85% yield). Anal. Calcd for $C_{37}H_{46}AlNO$: C, 81.13; H, 8.46. Found: C, 80.84; H, 8.32. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.19−7.10 (m, 15H, C*Ph*$_3$), 6.98 (br. s, 1H, O−*Ph*), 6.73 (br. s, 1H, O−*Ph*), 3.67 (s, 2H, Ph−CH_2), 2.27 (s, 6H, N*Me*$_2$), 2.15 (s, 3H, Ph−*Me*), 1.48 (septet, 2H, ^3J(HH) = 6.7 Hz, C*H* ^{i}Bu), 0.69 (d, 6H, ^3J(HH) = 6.4 Hz, CH_3 ^{i}Bu), 0.64 (d, 6H, ^3J(HH) = 6.4 Hz, CH_3 ^{i}Bu), −0.39 (dd, 2H, ^2J(HH) = 14.1 Hz, ^3J(HH) = 7.3 Hz, CH_2 ^{i}Bu), −0.45 (dd, 2H, ^2J(HH) = 14.1 Hz, ^3J(HH) = 7.3 Hz, CH_2 ^{i}Bu). ^{13}C{^{1}H}

(11) (a) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440. (b) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem* **2000**, *65*, 3090.

(12) Schorigin, P. *Chem. Ber.* **1927**, *60*, 8.

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NMR (100 MHz, CD_2Cl_2): δ 155.1 (O−*Ph*), 146.2 (Ph), 135.7 (Ph), 131.8 (Ph), 130.7 (Ph), 128.8 (Ph), 126.5 (Ph), 124.6 (Ph), 123.9 (Ph), 120.4 (Ph), 63.0 (*C*Ph$_3$), 62.5 (Ph*C*H$_2$), 44.3 (N*Me*$_2$), 27.6(0) (*C*H$_3$ ^{i}Bu), 27.5(8) (*C*H$_3$ ^{i}Bu), 25.3 (*C*H ^{i}Bu), 20.2 (br, *C*H$_2$ ^{i}Bu), 20.1 (*Me*Ph).

[{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(^{i}Bu)(NMe$_2$Ph)][HB(C$_6$F$_5$)$_3$] (3). In a small Schlenk tube, the diisobutyl Al complex **2** (120.0 mg, 0.219 mmol) and NMe$_2$Ph (26.5 mg, 0.219 mmol) were dissolved in 1 mL of CH_2Cl_2 to yield a colorless solution. B(C$_6$F$_5$)$_3$ (112.1 mg, 0.219 mmol) was then added at room temperature all at once, provoking gas formation (isobutene) for a few seconds. The resulting pale yellow solution was then stirred at room temperature for 1 h and was evaporated. Trituration of the colorless foamy residue with cold pentane caused the precipitation of a colorless solid which, after filtration and further drying under vacuum, was revealed to be the salt compound **3** (151 mg, 84% yield).[13] ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.35−7.19 (m, 15H, CPh$_3$), 7.01 (br s, 1H, O−*Ph*), 6.66 (br. s, 1H, O−*Ph*), 4.15 (br. d, 1H, *H*B), 3.33 (d, ^2J(HH) = 14.9 Hz, 1H, Ph−C*H*$_2$), 2.78 (d, ^2J(HH) = 14.5 Hz, 1H, Ph−C*H*$_2$), 2.77 (s, 3H, Me−Ph or N*Me*), 2.47 (s, 3H, *Me*−Ph or N*Me*), 2.39 (s, 3H, *Me*−Ph or N*Me*), 2.24 (s, 3H, *Me*−Ph or N*Me*), 2.14 (*Me*−Ph or N*Me*), 1.47 (septet, 2H, ^3J(HH) = 6.5 Hz, CH ^{i}Bu), 0.68 (d, 6H, ^3J(HH) = 5.8 Hz, C*H*$_3$ ^{i}Bu), 0.57 (d, 6H, ^3J(HH) = 6.5 Hz, C*H*$_3$ ^{i}Bu), 0.06 (d, 2H, ^3J(HH) = 7.3 Hz, CH$_2$ ^{i}Bu). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2):[14] δ 151.3 (O−C$_{ipso}$ Ph), 147.9 (d, ^2J(CF) = 235 Hz, *C*$_6$F$_5$), 145.8 (Ph), 143.7 (C$_{ipso}$ PhNMe$_2$), 136.5 (Ph), 136.3 (d, ^2J(CF) = 235 Hz, C$_6$F$_5$), 133.6 (Ph), 130.6 (Ph), 130.3 (Ph), 129.3 (Ph), 128.8 (Ph), 127.3 (Ph), 126.6 (Ph), 125.8 (Ph), 120.0 (Ph), 118.8 (Ph), 62.8 (*C*Ph$_3$ and Ph*C*H$_2$), 46.5 (N*Me*), 46.3 (N*Me*), 45.2 (N*Me*), 45.1 (N*Me*), 27.1 (CH$_3$ ^{i}Bu), 26.0 (CH$_3$ ^{i}Bu), 23.4 (CH ^{i}Bu), 20.0 (*Me*Ph), 16.1 (br, CH$_2$ ^{i}Bu). ^{11}B NMR (128.4 MHz, C_6D_6): δ −25.7 (d, ^2J(BH) = 54 Hz). ^{19}F NMR (376.5 MHz, C_6D_6): δ 133.2 (m, 2F, C$_6$*F*$_5$), −164.2 (t, 1F, C$_6$*F*$_5$), −167.3 (m, 2F, C$_6$*F*$_5$).

{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(O−CH$_2$Ph)(^{i}Bu) (4). In a glovebox, a stoichiometric amount of the diisobutyl Al complex **2** (33.5 mg, 0.061 mmol) and benzaldehyde (5.5 μL, 0.061 mmol) were added to CH_2Cl_2 (3 mL) in a sample vial to yield a colorless solution. With vigorous stirring, 0.05 equiv of B(C$_6$F$_5$)$_3$ (1.6 mg, 0.003 mmol) was then added to the solution. The mixture was stirred for 5 h at room temperature, after which it was evaporated to dryness under vacuum to yield a colorless solid. This solid was treated with pentane (5 mL) to wash off B(C$_6$F$_5$)$_3$ to afford, after drying, complex **4** in a pure form (24.4 mg, 67% yield). Anal. Calcd for $C_{40}H_{44}AlNO_2$: C, 80.37; H, 7.42. Found: C, 80.51; H, 7.21. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.28−7.11 (m, 20H, C*Ph*$_3$ and OCH$_2$*Ph*), 7.02 (br s, 1H, O−*Ph*), 6.72 (br. s, 1H, O−*Ph*), 4.37 (AB system, ^2J(HH) = 14.9 Hz, 2H, O−C*H*$_2$Ph), 4.00 (d, ^2J(HH) = 13.8 Hz, 1H, Ph−C*H*$_2$), 3.18 (d, ^2J(HH) = 13.9 Hz, 1H, Ph−C*H*$_2$), 2.46 (s, 3H, *Me*−Ph or N*Me*), 2.16 (s, 3H, *Me*−Ph or N*Me*), 2.15 (s, 3H, *Me*−Ph or N*Me*), 1.47 (septet, 2H, ^3J(HH) = 6.2 Hz, C*H* ^{i}Bu), 0.73 (d, 6H, ^3J(HH) = 6.5 Hz, C*H*$_3$ ^{i}Bu), 0.66 (d, 6H, ^3J(HH) = 6.5 Hz, C*H*$_3$ ^{i}Bu), −0.25 (dd, 2H, ^2J(HH) = 13.8 Hz, ^3J(HH) = 7.0 Hz, C*H*$_2$ ^{i}Bu), −0.42 (dd, 2H, ^2J(HH) = 13.9 Hz, ^3J(HH) = 7.1 Hz, C*H*$_2$ ^{i}Bu). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 154.6 (O−*C*$_{ipso}$ Ph), 148.2 (*C*$_{ipso}$ *Ph*$_2$CHO), 146.1 (*C*$_{ipso}$ C*Ph*$_3$), 144.9 (*C*$_{ipso}$ *Ph*CH$_2$−O), 135.8 (*C*$_{quat}$ *Ph*O), 131.6 (*C*H Ph), 130.7 (*C*H C*Ph*$_3$), 128.7 (*C*H Ph), 128.4 (*C*H Ph), 127.4 (*C*H Ph), 126.5 (*C*H C*Ph*$_3$), 125.5 (*C*H Ph), 125.4 (*C*H Ph), 124.6 (*C*$_{quat}$ *Ph*O), 120.5 (*C*$_{quat}$ *Ph*O), 64.0 (Ph*C*H$_2$N or Ph*C*H$_2$O), 63.0 (*C*Ph$_3$), 61.8 (Ph*C*H$_2$N or Ph*C*H$_2$O), 45.0 (N*Me*), 42.3 (N*Me*), 42.4 (N*Me*), 27.3 (*C*H$_3$ ^{i}Bu), 27.1 (*C*H$_3$ ^{i}Bu), 24.9 (*C*H ^{i}Bu), 20.1 (*Me*Ph), 15.3 (br, *C*H$_2$ ^{i}Bu).

{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(O−CHPh$_2$)(^{i}Bu) (5). The Al complex **5** was synthesized by following the same experimental procedure as that for complex **4**, using equimolar amounts of compound **2** (80.0 mg, 0.146 mmol) and benzophenone (26.6 mg, 0.146 mmol) and 0.05 equiv of B(C$_6$F$_5$)$_3$ (3.7 mg, 0.007 mmol), and was isolated in pure form as a colorless solid (53 mg, 54% yield). Anal. Calcd for $C_{46}H_{48}AlNO_2$: C, 81.99; H, 7.18. Found: C, 81.23; H, 7.13. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.33−6.82 (m, 26H, aromatics), 6.63 (br s, 1H, O−*Ph*), 5.36 (s, 1H, O−C*H*Ph$_2$), 3.56 (d, ^2J(HH) = 13.8 Hz, 1H, O−C*H*$_2$Ph), 2.93 (d, ^2J(HH) = 13.8 Hz, 1H, Ph−C*H*$_2$), 2.28 (s, 3H, *Me*−Ph or N*Me*), 2.16 (s, 3H, *Me*−Ph or N*Me*), 2.07 (s, 3H, *Me*−Ph or N*Me*), 1.38 (septet, 2H, ^3J(HH) = 7.2 Hz, C*H* ^{i}Bu), 0.67 (d, 6H, ^3J(HH) = 6.4 Hz, C*H*$_3$ ^{i}Bu), 0.54 (d, 6H, ^3J(HH) = 6.6 Hz, C*H*$_3$ ^{i}Bu), −0.36 (dd, 1H, ^2J(HH) = 14.0 Hz, ^3J(HH) = 6.8 Hz, C*H*$_2$ ^{i}Bu), −0.52 (dd, 1H, ^2J(HH) = 14.0 Hz, ^3J(HH) = 7.9 Hz, C*H*$_2$ ^{i}Bu). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 154.5 (O−*C*$_{ipso}$ Ph), 148.2 (*C*$_{ipso}$ *Ph*$_2$CHO), 148.0 (*C*$_{ipso}$ *Ph*$_2$-CHO), 146.1 (*C*$_{ipso}$ C*Ph*$_3$), 135.7 (*C*$_{quat}$ *Ph*O), 131.5 (*C*H Ph), 130.7 (*C*H Ph), 128.6 (*C*H Ph), 127.6 (*C*H Ph), 127.3 (*C*H Ph), 126.6 (*C*H Ph), 126.2 (*C*H Ph), 125.8 (*C*H−Ph), 125.7 (*C*H Ph), 125.6 (*C*H Ph), 124.8 (*C*H Ph), 124.6 (*C*$_{quat}$ *Ph*O), 120.7 (*C*$_{quat}$ *Ph*O), 75.2 (*C*HPh$_2$), 63.0 (*C*Ph$_3$), 61.4 (Ph*C*H$_2$), 46.5 (N*Me*), 44.8 (N*Me*), 42.4 (N*Me*), 27.5 (*C*H$_3$ ^{i}Bu), 27.0 (*C*H$_3$ ^{i}Bu), 24.9 (*C*H ^{i}Bu), 20.1 (*Me*Ph), 15.8 (br, *C*H$_2$ ^{i}Bu).

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Supporting Information Available: A CIF file giving crystallographic data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) We were unable to obtain a satisfactory elemental analysis for this salt compound.

(14) One ^{13}C NMR *C*$_6$F$_5$ resonance is not listed. It is most likely obscured by the other resonances in the aromatic region.

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