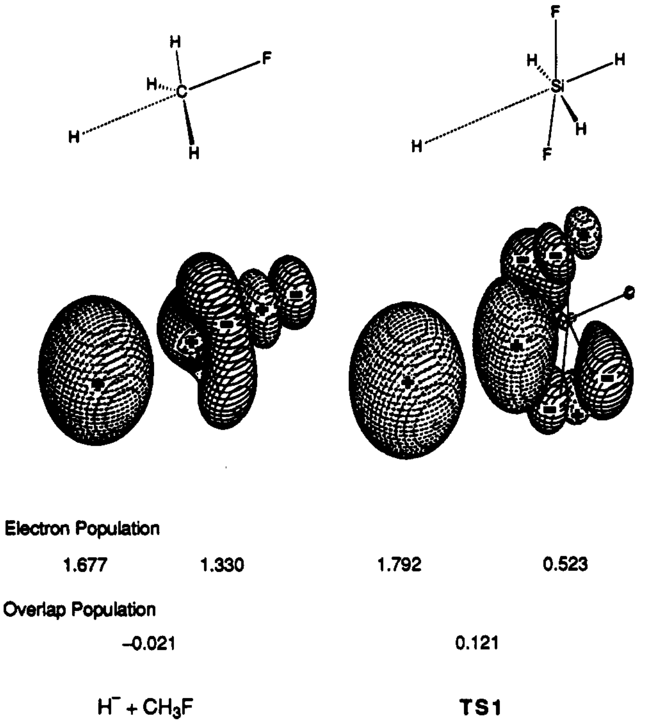

Figure 9. Comparison of the interactions in **TS1** and in a model S_N2 type reaction in terms of the paired interacting orbitals.

$SiH_3F_2^-$ are then represented practically in terms of an orbital pair that is presented in Figure 9. The interacting orbital of the $SiH_3F_2^-$ fragment shows a large amplitude at the silicon center and overlaps in-phase with the H^- orbital. The electron populations of these orbitals indicate that orbital interactions take place mainly between the occupied MO of H^- and the unoccupied canonical MO's of $SiH_3F_2^-$. A part of the electronic charge has been shifted from H^- to $SiH_3F_2^-$. This forms a marked contrast to the interaction between CH_3F and H^-, in which electron delocalization between the occupied MO of H^- and the unoccupied MO's of CH_3F is counterbalanced by the overlap repulsion between the occupied MO's of the two species.

Conclusion

In experiments, we find various combinations of ligands in silicon species. There may naturally be a variety of reaction mechanisms. The present analysis on a simplified reaction model does not necessarily exclude the concerted mechanism but has revealed an interesting aspect of chemical interactions between pentacoordinated silicon species and nucleophiles. It has been demonstrated that pentacoordinated silicon species have a strong ability to accept the attacking nucleophile without breaking the bond with the leaving group. It seems to be reasonable, therefore, to assume hexacoordinated species as the transition state or reaction intermediate in the ligand substitution reactions of silicon compounds.

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Sterically Crowded Aryloxide Compounds of Aluminum: Reactions with Main-Group Chlorides

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The interaction of $AlR(BHT)_2$ and $AlR_2(BHT)(OEt_2)$ (R = Me, Et) with main-group chlorides Me_3SnCl, $SnCl_2$, BCl_3, $AlCl_3$, $InCl_3$, and $ZnCl_2$, in pentane, Et_2O, or MeCN, leads to the formation of the aluminum chloride compounds $AlCl(BHT)_2$ (**1**), $AlCl(BHT)_2(OEt_2)$ (**2**), $AlClMe(BHT)(OEt_2)$ (**3**), $AlClEt(BHT)(OEt_2)$ (**4**), $AlCl_2(BHT)(OEt_2)$ (**5**), $[Al(\mu\text{-}Cl)Me(BHT)]_2$ (**6**), and $AlCl(BHT)_2(NCMe)$ (**8**). In contrast, the reaction of $AlMe(BHT)_2$ with $AlCl_3$ in CH_2Cl_2 results in Friedel–Crafts alkylation by "CH_2Cl" at the 4-position of BHT to give the substituted cyclohexadien-1-one **7**. The kinetics of this reaction have been investigated. The reaction of $AlMe(BHT)_2$ with 2 equiv of 2,6-Me_2pyHCl yields the ionic complex [2,6-Me_2pyH]-$[AlCl_2(BHT)_2]$ (**9**). The molecular structures of **5**, **6**, and **9** have been determined by X-ray crystallography. Crystal data for **5**: monoclinic, $P2_1/n$, a = 10.796 (2) Å, b = 17.753 (3) Å, c = 11.343 (2) Å, β = 97.36 (1)°, Z = 4, R = 0.067, R_w = 0.078. Crystal data for **6**: monoclinic, $P2_1/n$, a = 10.410 (6) Å, b = 9.865 (3) Å, c = 16.42 (1) Å, β = 97.20 (5)°, Z = 2, R = 0.069, R_w = 0.088. Crystal data for **9**: triclinic, $P\bar{1}$, a = 9.3799 (8) Å, b = 13.898 (1) Å, c = 14.8255 (14) Å, α = 101.900 (8)°, β = 91.080 (7)°, γ = 98.050 (7)°, Z = 2, R = 0.050, R_w = 0.062.

Introduction

The halodealumination of organoaluminum compounds by main-group halides (eq 1) is a class of reaction of industrial significance.[2] The method has been successful

$$\mathrm{MX}_n \xrightarrow[-\mathrm{AlXR}_2]{\mathrm{AlR}_3} \mathrm{MX}_{n-1}\mathrm{R} \xrightarrow{(n-1)\mathrm{AlR}_3} \mathrm{MR}_n \qquad (1)$$

for the preparation of organo compounds of, among others, zinc, mercury,[3] boron,[4] gallium,[5] germanium,[6] tin,[7] and lead.[8,9] The aluminum alkyl chloride coproduct formed

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(1) (a) Harvard University. (b) University of California, Irvine.

(2) For a summary see: Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1983; Vol. 1, Chapter 6, and references therein.

(3) Pasynkiewicz, S. *Przem. Chem.* **1960**, *39*, 225.

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often has commercial value. For example, $AlClEt_2$, formed in the preparation of $ZnEt_2$ (eq 2), is recovered and sold as a Ziegler catalyst component. Additionally, the reaction of $AlCl_3$ with aluminum alkyls has been employed in the synthesis of many alkylaluminum chlorides.[10]

$$2AlEt_3 + ZnCl_2 \rightarrow ZnEt_2 + 2AlClEt_2 \quad (2)$$

The generality of the halodealumination reaction has prompted us to investigate the interaction of $AlR(BHT)_2$ and $AlR_2(BHT)(OEt_2)$ (R = Me, Et) with a variety of main-group chlorides as a facile route to the chloroaluminum aryloxide derivatives. The results of this study are presented herein.

Results and Discussion

Trimethyltin Chloride. Lappert and Horder have briefly reported that the metathetical reaction between Me_3SnCl and aluminum alkyl chlorides (e.g., eq 3) occurs readily even in the presence of coordinating solvents, such as Et_2O.[11]

$$2Me_3SnCl + (AlClEt_2)_2 \rightarrow 2Me_3SnEt + (AlCl_2Et)_2 \quad (3)$$

The interaction of Me_3SnCl with either $AlMe(BHT)_2$ or $AlEt(BHT)_2$, in pentane, results in the rapid precipitation of the base-free monochloride $AlCl(BHT)_2$ (1; eq 4), which may be isolated by immediate removal of the solvent and tin coproducts.[12] Extended reaction (ca. 10 min) leads to

$$AlR(BHT)_2 + Me_3SnCl \xrightarrow[\text{pentane, R = Me, Et}]{} \underset{\mathbf{1}}{AlCl(BHT)_2} + Me_3SnR \quad (4)$$

the clear solution turning deep red. Removal of volatiles from this deep red solution leads to the isolation of a mixture of BHT-H[13] and several unidentified species.

Compound **1** is very unstable and decomposes, even under an inert atmosphere in the solid state. However, addition of Et_2O to **1** allows for the isolation of the Lewis acid–Lewis base complex $AlCl(BHT)_2(OEt_2)$ (**2**), which is stable in the solid state, under an inert atmosphere, for a period of weeks.

The reaction of 1 equiv of Me_3SnCl with $AlR_2(BHT)(OEt_2)$[14] in pentane leads to $AlClR(BHT)(OEt_2)$ (R = Me (**3**), Et (**4**)) in good yield (eq 5). N.B. Compound **3** is also

$$AlR_2(BHT)(OEt_2) + Me_3SnCl \rightarrow AlClR(BHT)(OEt_2) + Me_3SnR \quad (5)$$
$$R = Me\ (\mathbf{3}),\ Et\ (\mathbf{4})$$

$$AlMe_2Cl + BHT\text{-}H \xrightarrow[Et_2O]{} AlClMe(BHT)(OEt_2) + MeH \quad (6)$$

formed from the reaction of BHT-H with $AlMe_2Cl$ in Et_2O (eq 6). Use of 2 equiv of Me_3SnCl leads to the dichloride compound $AlCl_2(BHT)(OEt_2)$ (**5**), also in high yield (eq 7).

$$AlR_2(BHT)(OEt_2) + 2Me_3SnCl \rightarrow \underset{\mathbf{5}}{AlCl_2(BHT)(OEt_2)} + 2Me_3SnR \quad (7)$$

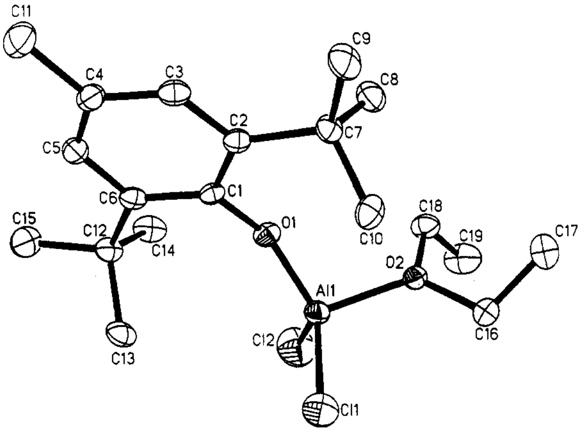

Figure 1. Molecular structure of $AlCl_2(BHT)(OEt_2)$ (**5**). Thermal ellipsoids are shown at the 50% level, and hydrogen atoms have been omitted for clarity.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) in $AlCl_2(BHT)(OEt_2)$ (5)

Al(1)–Cl(1)	2.110 (2)	Al(1)–Cl(2)	2.104 (2)
Al(1)–O(1)	1.700 (2)	Al(1)–O(2)	1.873 (2)
O(1)–C(1)	1.367 (4)	O(2)–C(16)	1.416 (4)
O(2)–C(18)	1.469 (4)		
Cl(1)–Al(1)–Cl(2)	110.1 (1)	Cl(1)–Al(1)–O(1)	115.5 (1)
Cl(1)–Al(1)–O(2)	106.8 (1)	Cl(2)–Al(1)–O(1)	116.7 (1)
Cl(2)–Al(1)–O(2)	101.5 (1)	O(1)–Al(1)–O(2)	104.1 (1)
Al(1)–O(1)–C(1)	154.4 (2)	Al(1)–O(2)–C(16)	125.6 (2)
Al(1)–O(2)–C(18)	117.3 (2)	C(16)–O(2)–C(18)	115.7 (2)

The mono-BHT compounds **3**–**5** are significantly more stable than their corresponding bis-BHT derivative **2**, since once they are isolated they may be stored, under an inert atmosphere, at room temperature indefinitely.

The molecular structure of **5** has been determined by X-ray crystallography and is shown in Figure 1; selected bond lengths and angles are given in Table I. The structure consists of discrete monomeric units with no unusual bond lengths or angles. The Al–Cl bond distances in **5** are within the range reported for terminal chloride ligands.[15] While the Al–O distance associated with the BHT ligand is consistent with our previous observations,[16] that associated with Et_2O (1.873 (2) Å) is slightly shorter than those previously observed (1.89 (1)–1.97 (1) Å) for

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(12) The identification of the tin coproducts as Me_3SnR (R = Me, Et) was determined by mass spectrometry.

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Table II. Selected Bond Lengths (Å) and Bond Angles (deg) in $[Al(\mu\text{-}Cl)Me(BHT)]_2$ (6)

Al(1)–Cl(1)	2.277 (3)	Al(1)–O(1)	1.672 (4)
Al(1)–C(16)	1.920 (8)	Al(1)–Cl(1A)	2.291 (3)
O(1)–C(1)	1.367 (6)		
Cl(1)–Al(1)–O(1)	106.5 (1)	Cl(1)–Al(1)–C(16)	109.6 (2)
Cl(1)–Al(1)–Cl(1A)	89.1 (1)	O(1)–Al(1)–C(16)	127.7 (3)
O(1)–Al(1)–Cl(1A)	109.1 (1)	C(16)–Al(1)–Cl(1A)	108.1 (2)
Al(1)–Cl(1)–Al(1A)	90.9 (1)	Al(1)–O(1)–C(1)	154.1 (3)

diethyl ether complexes of alkyl and hydride compounds.[17] This is as would be expected for a highly Lewis acidic dichloro complex.

We have previously prepared the trimethylamine analogues of **2** and **3**, from the reaction of Me_3NHCl with $AlMe(BHT)_2$ and $AlMe_2(BHT)(OEt_2)$, respectively.[16a] However, addition of 2 equiv of Me_3NHCl to $AlMe_2(BHT)(OEt_2)$ did not yield the NMe_3 analogue of **5** but rather the ionic complex $[Me_3NH][AlCl_2Me(BHT)]$.[16a]

Tin(II) Chloride. The metal(II) halides of tin and lead have been shown to react with aluminum trialkyls to yield an equimolar mixture of the tetraalkyl species MR_4 and the metal.[11] This reaction presumably proceeds via the disproportionation of an unstable metal(II) dialkyl.

The reaction of $SnCl_2$ with 1 equiv of $AlR(BHT)_2$ (R = Me, Et) in Et_2O leads to the formation of a deep red-orange suspension. Removal of the solvent in vacuo, extraction with toluene, filtration, and removal of solvent leads to a high yield (76–85%) of **2** (eq 8). Unlike the case for the reactions with Me_3SnCl, we were unable to characterize the tin-containing side products or obtain clean reactions with $AlR_2(BHT)(OEt_2)$ (R = Me, Et).

$$AlR(BHT)_2 + SnCl_2 \xrightarrow[Et_2O]{} AlCl(BHT)_2(OEt_2) + \text{tin-containing products} \quad (8)$$

Boron Trichloride. The reaction of $AlMe(BHT)_2$ with 1 molar equiv of BCl_3 in a pentane/hexane mixture does not result in alkyl–halide exchange, as might be expected, but aryloxide–halide exchange (eq 9). Although there are no examples reported of BHT acting as a bridging ligand between two group 13 elements, such a species, $Al(\mu\text{-}BHT)B$, is clearly implicated in eq 9. The dimeric aluminum-containing product $[Al(\mu\text{-}Cl)Me(BHT)]_2$ (**6**) was isolated by fractional crystallization, while the boron-containing species $BCl_2(BHT)$ was isolated as an impure yellow oil and was found to be identical with an authentic sample.[18] Compound **6**, previously prepared by the more convenient reaction of $AlMe_2Cl$ with BHT-H (eq 10),[19] was proposed to be dimeric on the basis of molecular weight measurements. We have, by X-ray crystallographic analysis, confirmed that, in the solid state, **6** does indeed exist as a chloride-bridged dimer.

$$AlMe(BHT)_2 + BCl_3 \rightarrow AlClMe(BHT) + BCl_2(BHT) \quad (9)$$

$$AlMe_2Cl + BHT\text{-}H \rightarrow \tfrac{1}{2}[Al(\mu\text{-}Cl)Me(BHT)]_2 + MeH \quad (10)$$

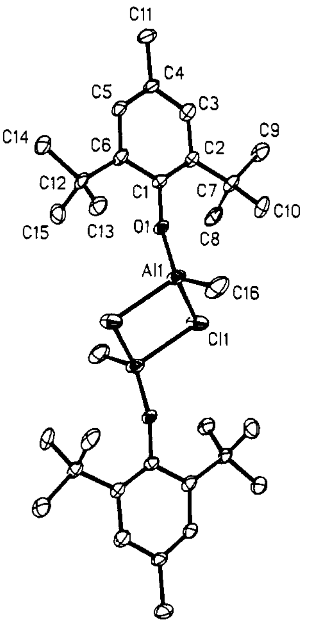

Figure 2. Molecular structure of $[Al(\mu\text{-}Cl)Me(BHT)]_2$ (**6**). Thermal ellipsoids are shown at the 40% level, and hydrogen atoms have been omitted for clarity.

The molecular structure of **6** is shown in Figure 2; selected bond lengths and angles are given in Table II. Compound **6** exists as discrete dimers with no short intramolecular distances between the dimeric units. The aryloxide Al(1)–O(1) bond distance (1.672 (4) Å) is significantly shorter than those observed previously for four-coordinate Al–BHT systems (1.713 (4)–1.754 (1) Å). The bridging Al–Cl bond distances (2.277 (3) and 2.291 (3) Å) are, as expected, slightly longer than those found for the terminal chlorides in the monomeric analogue of **6**, i.e., $[AlMeCl_2(BHT)]^-$ (2.199 (2) and 2.190 (2) Å).[16a] Compared with those of other bridging chloride compounds, the Al–Cl distances in **6** are similar to those in $[MeAlCl_2]_2$ (2.25 and 2.26 Å)[20] and $[(Me)_2AlCl]_2$ (2.31 Å)[21] and shorter than those found in $[(\eta^3\text{-}C_5Me_5)Al(Cl)Me]_2$ (2.378 (3) and 2.398 (2) Å).[22] The Al_2Cl_2 core is planar, and symmetric within the limits of the data.

Aluminum Trichloride. The reaction of $AlMe(BHT)_2$ with $AlCl_3$ is highly solvent-dependent. Reaction of $AlMe(BHT)_2$ with 1 equiv of $AlCl_3$ in pentane leads to a complex mixture of products, including a large quantity of BHT-H,[13] indicative of decomposition. In Et_2O this reaction also yields multiple products; however, from ^1H NMR spectra compounds **3** and **5** were determined to be the major constituents. Pure **5** can be isolated by fractional crystallization from CH_2Cl_2. The pathway for the formation of these compounds is probably similar to that for BCl_3 with $AlMe(BHT)_2$, i.e., chloride–aryloxide ligand exchange, via an asymmetric dimer (eq 11). Dimeric aluminum compounds with unlike bridging groups were first observed by Mole et al.[23] The only examples that have been isolated involving a bridging BHT are the heterobimetallic compounds $(BHT)MeAl(\mu\text{-}BHT)(\mu\text{-}OR)LiOEt_2$; however, we note that bridging BHT ligands are commonly found for other metal systems.[24]

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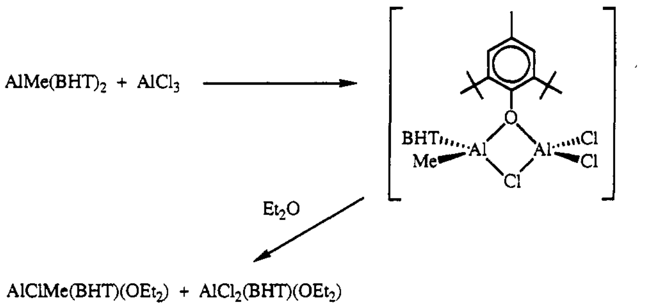
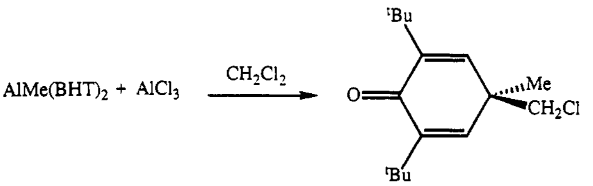


(11)

Reaction of $AlMe(BHT)_2$ with $AlCl_3$ in CH_2Cl_2 at room temperature leads, over the course of 12 h, to a light brown solution. Removal of solvent in vacuo gives a viscous dark brown oil. The ^1H NMR spectrum of this crude material indicates only one type of *tert*-butyl proton; however, the shift (δ 1.29) is inconsistent with the formation of BHT-H (δ 1.37) or starting material (δ 1.58). Hydrolysis of the reaction mixture with HCl/H_2O and extraction with Et_2O, followed by either crystallization from pentane or vacuum sublimation, afford a single product, $\mathrm{O{=}\overline{CC(^tBu){=}C(H)C(Me)(CH_2Cl)C(H){=}C}(^tBu)}$ (7; eq 12). Compound



(12)

7 has been fully characterized by IR and ^1H and ^{13}C NMR spectroscopy, elemental analysis, and mass spectrometry (see Experimental Section).[25] The structure has also been confirmed by X-ray crystallography[26] (see the supplementary material).

The stoichiometric nature of the formation of 7 (eq 12) was determined by ^1H NMR spectral analysis of the crude products from the reaction of $AlMe(BHT)_2$ with varying quantities of $AlCl_3$; i.e., the yield of 7 is directly proportional to the molar equivalents of $AlCl_3$ employed. Complete conversion of the BHT ligands in $AlMe(BHT)_2$ to 7 occurs with ca. 0.8 equiv of $AlCl_3$ (see below). N.B. No reaction is observed in the absence of $AlCl_3$ even in refluxing CH_2Cl_2.

The source of the chloromethyl group in 7 was confirmed as the CH_2Cl_2 solvent, by carrying the reaction out in CD_2Cl_2 and isolating the appropriately deuterated product, $\mathrm{O{=}\overline{CC(^tBu){=}C(H)C(Me)(CD_2Cl)C(H){=}C}(^tBu)}$ (7-d_2). The IR spectrum of 7-d_2 shows an insignificant shift in the carbonyl bands (1663 and 1646 cm^{-1} (7) versus 1668 and 1651 cm^{-1} (7-d_2)). The ^1H NMR spectra of 7 and 7-d_2 are identical except for the absence of the methylene resonance in the latter, while the singlet observed in the ^{13}C NMR spectrum of 7 for the methylene carbon is replaced by a quintet ($J(^{13}C-^2H)$ = 22.9 Hz).

Table III. Selected Kinetic Data for the Reaction of $AlMe(BHT)_2$ with $AlCl_3$ in CH_2Cl_2 at 298 K[a]

$[AlMe(BHT)_2]$, 10^{-2} mol L^{-1}	$[AlCl_3]$, 10^{-1} mol L^{-1}	$AlCl_3$:BHT	k_{obs},[b] s^{-1}
7.99	0.640	0.4	5.23×10^{-5}
8.15	0.896	0.55	2.12×10^{-4}
7.87	0.944	0.6	3.09×10^{-4}
8.08	1.075	0.665	3.75×10^{-4}
8.25	1.232	0.75	1.09×10^{-3}
8.17	1.635	1.0	4.63×10^{-3}

[a] See Experimental Section for conditions. [b] $-\delta[BHT]/\delta t = k_{obs}[BHT]$.

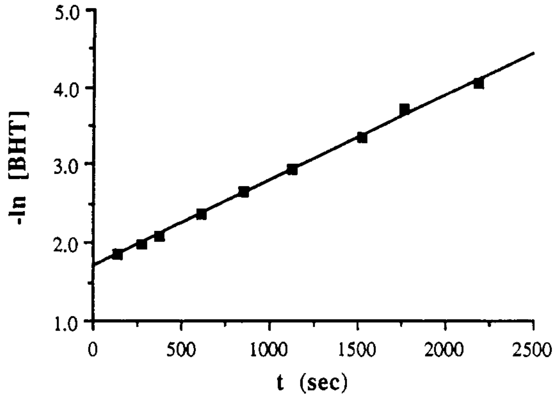
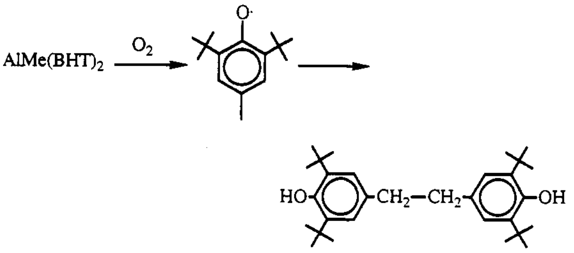


Figure 3. Representative first-order rate plot for the conversion of $AlMe(BHT)_2$ to 7 at 298 K ($[AlMe(BHT)_2] = 8.25 \times 10^{-2}$ mol L^{-1}, $[AlCl_3] = 1.232 \times 10^{-1}$ mol L^{-1}, $k_{obs} = 1.09 \times 10^{-3}$ s^{-1}, $R = 0.998$).

Until recently the reactivity of coordinated BHT has been limited to oxidation reactions, e.g., radical coupling of two BHT moieties at the methyl in the 4-position (eq 13).[27]



(13)

The dissolution of $AlCl_3$ in alkyl halides is known to result in the formation of conducting solutions,[28] from which a number of workers have proposed that, depending on the nature of the alkyl (R) group, either complexation (I) or ionization (II) of the alkyl chloride occurs (i.e., eq 14).[29] Where R is capable of forming a particularly stable

$$RCl + AlCl_3 \rightleftharpoons \underset{I}{R^{\delta+}Cl{\cdots}Al^{\delta-}Cl_3} \rightleftharpoons \underset{II}{[R]^+[AlCl_4]^-} \qquad (14)$$

carbonium ion, it is probable that the attacking electrophile in alkylation is the actual carbonium ion (cf. II). In other cases it seems likely that the attacking electrophile is a polarized complex (cf. I). Either pathway is compatible with the commonly observed rate law (eq 15),[30] where ArH is the aromatic substrate and RX the alkyl halide.

$$\text{rate} = k[ArH][RX][AlCl_3] \qquad (15)$$

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[24] (a) Calabrese, J.; Cushing, M. A., Jr.; Ittel, S. D. *Inorg. Chem.* **1988**, *27*, 867. (b) Çetinkaya, B.; Gümrükçü, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2086.

[25] For previous syntheses of substituted cyclohexadien-1-ones see for example: (a) Baird, R.; Winstein, S. *J. Am. Chem. Soc.* **1962**, *84*, 788. (b) Miller, B.; Margulies, H. *J. Org. Chem.* **1965**, *30*, 3895. (c) Kornblum, M.; Seltzer, R. *J. Am. Chem. Soc.* **1961**, *83*, 3668.

[26] Crystal data for 7: monoclinic, $P2_1/c$, $a = 6.323$ (2) Å, $b = 15.368$ (9) Å, $c = 15.865$ (7) Å, $\beta = 99.45$ (3)°, $V = 1616$ (1) Å^3, $Z = 4$, D(calcd) = 1.104 g cm^{-3}, λ(Mo Kα) = 0.71073 cm^{-1}, $T = 253$ K, 1572 reflections collected ($4.0 < 2\theta < 40.0°$), 1267 independent and 559 observed ($F > 6.0\sigma(F)$), $R = 0.121$, $R_w = 0.132$.

[27] Skowrońska-Ptasińska, M.; Starowieyski, K. B.; Pasynkiewicz, S. *J. Organomet. Chem.* **1977**, *141*, 149.

[28] Wertyporoch, E.; Firla, T. *Z. Phys. Chem.* **1932**, *162*, 398.

[29] See for example: (a) Walker, J. W. *J. Chem. Soc.* **1904**, *84*, 1082. (b) Dougherty, G. *J. Am. Chem. Soc.* **1929**, *51*, 576. (c) Whitmore, F. C. *J. Am. Chem. Soc.* **1932**, *54*, 3274.

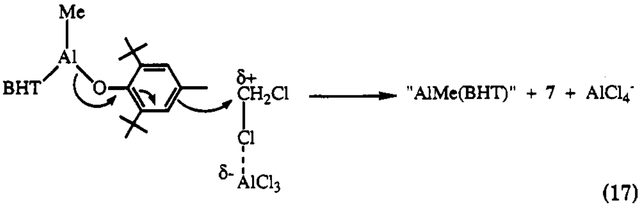
[30] (a) Olah, G. A.; Kuhn, S. J.; Flood, S. H. *J. Am. Chem. Soc.* **1962**, *84*, 1688. (b) Olah, G. A.; Flood, S. H.; Moffatt, M. E. *J. Am. Chem. Soc.* **1964**, *86*, 1060. (c) Olah, G. A.; Kobayashi, S.; Tashiro, M. *J. Am. Chem. Soc.* **1972**, *94*, 7448.

When an excess of $AlMe(BHT)_2$ was allowed to react with $AlCl_3$ in CH_2Cl_2 solution, the BHT ligand, as determined by the GC analysis of hydrolyzed aliquots (see Experimental Section), disappeared in a first-order fashion (i.e., eq 16). First-order observed rate constants, k_{obs}

$$\frac{-\delta[\mathrm{BHT}]}{\delta t} = k_{obs}[\mathrm{BHT}] \qquad (16)$$

(Table III), were calculated from the corresponding plot of $-\ln$ [BHT] versus time (e.g., Figure 3). A plot of k_{obs} versus [$AlCl_3$] does not show the expected first-order dependence on the Lewis acid. This deviation from the expected dependence is consistent with the presence of a number of competing side reactions involving $AlCl_3$.

(i) If we assume that the first step of the Friedel–Crafts alkylation of the coordinated BHT ligands in $AlMe(BHT)_2$ is the formation of either the carbocation (cf. II) or the polarized complex (cf. I), then the subsequent reaction involves electrophilic attack on $AlMe(BHT)_2$ (e.g., eq 17).



(17)

It is highly unlikely that the cationic aluminum fragment will be as written, and either chloride abstraction from or complexation with $AlCl_4^-$ will occur (i.e., eq 18). It is also

$$\text{“AlMe(BHT)”} + AlCl_4^- \rightarrow (BHT)MeAl(\mu\text{-}Cl)_2AlCl_2 \rightleftharpoons AlClMe(BHT) + AlCl_3 \qquad (18)$$

possible that this may occur in a concerted manner during the alkylation reaction. The subsequent reaction of AlClMe(BHT) with $CH_2Cl_2/AlCl_3$ (see Experimental Section) will presumably lead, in addition to 7, to the formation of $AlCl_2Me$, which will complex with $AlCl_3$ (eq 19).[31] The presence of the equilibrium shown in eqs 18 and 19 will, therefore, reduce the availability of free $AlCl_3$ for reaction with CH_2Cl_2 (eq 14).

$$AlCl_2Me + AlCl_3 \rightleftharpoons MeClAl(\mu\text{-}Cl)_2AlCl_2 \qquad (19)$$

(ii) We have already shown that in Et_2O solution $AlMe(BHT)_2$ reacts with $AlCl_3$ to yield compounds **3** and **5** (eq 11). It is reasonable to propose that a similar exchange reaction will occur in CH_2Cl_2, i.e., eq 20. While

$$AlMe(BHT)_2 + AlCl_3 \rightarrow AlClMe(BHT) + AlCl_2(BHT) \qquad (20)$$

$AlClMe(BHT)(OEt_2)$ does react with $CH_2Cl_2/AlCl_3$ to give **7** (see Experimental Section), in ca. 90% yield, $AlCl_2(BHT)(OEt_2)$ does not react under the conditions studied. In addition, there is no reaction between $AlCl_2(BHT)(OEt_2)$ and $AlMe(BHT)_2$ in CH_2Cl_2. Thus, if the rate of ligand exchange (i.e., eq 20) is greater than, or comparable to, the rate of Friedel–Crafts alkylation (eq 12), then not only will the concentration of $AlCl_3$ available as a catalyst be lowered but also a proportion of the BHT will be inert toward alkylation. This latter situation is indeed the case, since at low relative concentrations of $AlCl_3$ significant quantities of BHT-H are observed upon hydrolysis, despite extended reaction times (days).

Indium Trichloride. The reaction of $AlR(BHT)_2$ (R = Me, Et) with 1 equiv of $InCl_3$ in Et_2O leads to the formation of **2** in high yield, while the reaction of $AlMe(BHT)_2$ in MeCN yielded the complex $AlCl(BHT)_2(NCMe)$ (**8**; eq 21).

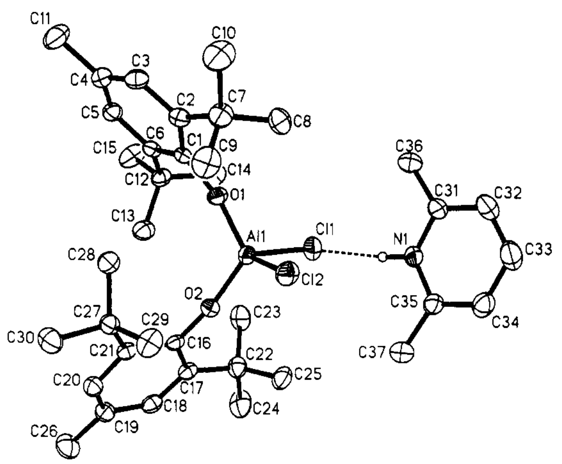
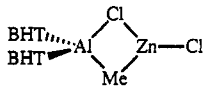


Figure 4. Structure of $[2,6\text{-}Me_2pyH][AlCl_2(BHT)_2]$ (**9**). Thermal ellipsoids are shown at the 50% level, and organic hydrogen atoms have been omitted for clarity.

$$AlMe(BHT)_2 + InCl_3 \rightarrow \underset{\mathbf{8}}{AlCl(BHT)_2(NCMe)} + \text{indium-containing products} \qquad (21)$$

Zinc Dichloride. The reaction of $AlMe(BHT)_2$ with $ZnCl_2$ in Et_2O is slow, resulting in only partial conversion to **2**, the remaining aluminum-containing product being $AlMe(BHT)_2(OEt_2)$. Given that this chloride–methyl exchange occurs, like those with group 13 chlorides discussed above, through a dimeric intermediate (i.e., III), then the lower Lewis acidity of zinc halides and alkyls as compared to B, Al, or In may explain the low reactivity.[32]



III

2,6-Dimethylpyridinium Chloride. Trialkylammonium chloride salts have successfully been used in the synthesis of group 3 chlorides from both hydrides and alkyls.[33] However, although the reaction of $AlMe(BHT)_2$ with Me_3NHCl does yield the monochloride compound, the trimethylamine liberated in the reaction coordinates to the aluminum.[16a] We reasoned, therefore, that the use of a sterically hindered "noncoordinating" amine e.g., $2,6\text{-}Me_2py$ should inhibit this complexation[34] and allow for the isolation of $AlCl(BHT)_2$.

The addition of 1 equiv of $2,6\text{-}Me_2pyHCl$ to $AlMe(BHT)_2$ does not yield either the free or even the complexed chloride as expected, but rather a moderate yield of the ionic complex $[2,6\text{-}Me_2pyH][AlCl_2(BHT)_2]$ (**9**; eq 22).

$$AlMe(BHT)_2 \rightarrow AlCl(BHT)_2 \rightarrow [AlCl_2(BHT)_2]^- \qquad (22)$$

If 2 equiv of $2,6\text{-}Me_2pyHCl$ is used, compound **9** is formed in essentially quantitative yield. The complexation of chloride to $AlCl(BHT)_2$ as opposed to further reaction with $AlMe(BHT)_2$ may be attributed to the higher Lewis acidity of aluminum chlorides versus that of alkyls.

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[31] Rytter, E.; Kvisle, S. *Inorg. Chem.* **1986**, *25*, 3796.

[32] (a) Sheverdina, I.; Kocheskov, K. A. *The Organic Compounds of Zinc and Cadmium*; North-Holland: Amsterdam, 1967. (b) Moseley, P. T.; Shearer, H. M. M. *J. Chem. Soc., Dalton Trans.* **1973**, 64.

[33] See, for example: Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1625 and references therein.

[34] Although $2,6\text{-}Me_2py$ does not form an adduct with $AlMe(BHT)_2$, the mono(aryloxide) complex $AlMe_2(BHT)(2,6\text{-}Me_2py)$ is readily isolated and has been crystallographically characterized.[16b]

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) in [2,6-Me_2pyH][$AlCl_2$(BHT)$_2$] (9)

Al(1)–Cl(1)	2.192 (1)	Al(1)–Cl(2)	2.166 (1)
Al(1)–O(1)	1.703 (2)	Al(1)–O(2)	1.705 (2)
O(1)–C(1)	1.356 (3)	O(2)–C(16)	1.362 (3)
Cl(1)–Al(1)–Cl(2)	100.3 (1)	Cl(1)–Al(1)–O(1)	104.8 (1)
Cl(1)–Al(1)–O(2)	112.4 (1)	Cl(2)–Al(1)–O(1)	115.0 (1)
Cl(2)–Al(1)–O(2)	105.8 (1)	O(1)–Al(1)–O(2)	117.4 (1)
Al(1)–O(1)–C(1)	165.9 (2)	Al(1)–O(2)–C(16)	169.9 (1)

The formation of chloroaluminate salts, such as 9 and [Me_3NH][$AlCl_2Me$(BHT)], is commonly observed in the reactions between $AlCl_3$ and MCl (M^+ being an alkali-metal ion or an organic cation).[35]

Crystals of 9 suitable for X-ray diffraction studies were obtained from CH_2Cl_2 solution. The molecular structure of 9 is shown in Figure 4; selected bond lengths and angles are given in Table IV. Although the proton associated with the pyridinium cation, H(1a), was not located but rather included using a riding model in the diffraction study, the orientation of the pyridinium with respect to Cl(1) (see Figure 4) and the N(1)···Cl(1) distance (3.218 (5) Å) are both consistent with the presence of a hydrogen bond. Thus, the structure consists of a discrete anion–cation pair, held together by a N–H···Cl hydrogen bond. The presence of a sharp signal in the ^1H NMR spectrum (δ 12.89) for the pyridinium proton suggests the retention of the hydrogen bonding in solution.

The geometry around aluminum is distorted from tetrahedral. As may be expected from steric considerations, the largest interligand angle is between the BHT groups (O(1)–Al(1)–O(2) = 117.4 (1)°) and the smallest is between the chlorides (Cl(1)–Al(1)–Cl(2) = 100.3 (1)°). The Al–O bond distances and the Al–O–C bond angles are in the range observed previously for aluminum–BHT complexes.[16] However, the Al–Cl distances are worthy of comment. Although both Al–Cl bond distances are within the range associated for terminal aluminum chlorides,[15] the Al(1)–Cl(1) bond (2.192 (1) Å) distance is slightly larger than Al(1)–Cl(2) (2.166 (1) Å), possibly as a result of the hydrogen-bonding interaction to the former. Similar asymmetric M–Cl bonding is observed in the solid-state structure of [Et_3NH][$InCl_2$(dpt)$_2$] (Hdpt = 1,3-diphenyltriazene), in which the longer of the two In–Cl distances is to the chloride involved in N–H···Cl hydrogen bonding.[36]

Experimental Section

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Melting points were determined in sealed capillaries and are uncorrected. IR spectra (4000–600 cm^{-1}) were recorded on a Nicolet DX-5 FTIR spectrometer as Nujol mulls on KBr plates. ^1H and ^{13}C NMR spectra, in C_6D_6, were recorded on Bruker AM-250, -400, and -500 spectrometers, and chemical shifts are reported versus internal C_6D_5H (δ 7.15, ^1H) and C_6D_6 (δ 128.00, ^{13}C), respectively. Mass spectra were recorded using a JEOL AX-505H mass spectrometer and associated data system. An electron beam energy of 70 eV was used, and all spectra were recorded at 1500 mass resolution. Reported *m/z* values are for the predominant ion within the isotope pattern for each signal. Gas chromatography was performed on a Perkin-Elmer 900 GC instrument using a Supelco SP-2100 column and flame ionization detection. All manipulations were carried out under nitrogen or argon. Solvents were dried, distilled, and degassed prior to use.

$AlMe_3$ (2.0 M solution in hexane) and $AlEt_3$ (1.0 M solution in hexane) were used as supplied (Aldrich). BHT-H, Me_3SnCl, $SnCl_2$, BCl_3 (hexane, 1 M), $AlCl_3$, and CD_2Cl_2 (Aldrich), $GaCl_3$ and $InCl_3$ (Strem), HCl (Matheson), and 2,6-dimethylpyridine (Eastman) were all used as received. $ZnCl_2$ (Mallinckrodt) was dried by heating in vacuo prior to use. The synthesis of AlMe(BHT)$_2$,[16a] AlEt(BHT)$_2$,[14] $AlMe_2$(BHT)(OEt_2),[14] and $AlEt_2$(BHT)(OEt_2)[14] were carried out according to literature methods, while 2,6-Me_2pyHCl was prepared by bubbling HCl through a pentane solution of 2,6-Me_2py.

AlCl(BHT)$_2$ (1). Method 1. AlMe(BHT)$_2$ (1.00 g, 2.08 mmol) was dissolved in pentane (30 mL), and Me_3SnCl (0.41 g, 2.06 mmol) was added under increased N_2 purge. The solution was stirred for 5 min as a white precipitate formed, after which the volume of solvent was reduced to approximately 15 mL, in vacuo. The remaining solvent was removed via cannula after the solid was allowed to settle. The resulting white solid was dried in vacuo for 5 min and all analysis performed immediately: yield ca. 30%. Storage at −20 °C inhibits decomposition; however, even under an inert atmosphere the solid decomposes rapidly (hours to days), becoming red.

Method 2: as with method 1 but with AlEt(BHT)$_2$; yield ca. 30%. Mp: 104–108 °C (dec pt 145 °C). IR: 1298 (m), 1264 (s), 1247 (s), 1213 (s), 1201 (sh), 1161 (sh), 1122 (s), 1038 (w), 1027 (w), 966 (s), 937 (s), 904 (s), 890 (s), 863 (sh), 856 (s), 772 (m), 722 (w), 678 (m), 647 (m), 618 (w), 575 (w), 501 (s) cm^{-1}. ^1H NMR: δ 7.13 (2 H, s, C_6H_2), 2.27 (3 H, s, CH_3), 1.60 (18 H, s, $C(CH_3)_3$). ^{13}C NMR: δ 151.84 (OC, BHT), 138.72 (*o*-C, BHT), 129.07 (*m*-C, BHT), 126.34 (*p*-C, BHT), 34.94 ($C(CH_3)_3$, BHT), 32.09 ($C(CH_3)_3$, BHT), 21.37 (CH_3, BHT). Mass spectrum: *m/z* 500 (M^+). Anal. Calcd for $C_{30}H_{46}AlClO_2$: C, 71.90; H, 9.25. Found: C, 70.24; H, 8.96.

AlCl(BHT)$_2$(OEt_2) (2). Method 1. To a pentane (100 mL) solution of AlMe(BHT)$_2$ (5.00 g, 10.4 mmol) was added $SnMe_3Cl$ (2.08 g, 10.4 mmol), and the solution was stirred at room temperature for 10 min. The precipitate thus formed was allowed to settle and the solution removed via cannula. To the solid was added Et_2O (50 mL), and the resulting solution was stirred for 12 h. Et_2O was removed under vacuum to give a white amorphous powder: yield >90%.

Method 2: as with method 1, but with AlEt(BHT)$_2$ (0.40 g, 0.81 mmol) and Me_3SnCl (0.16 g, 0.80 mmol); yield ca. 20%. No attempt was made to optimize the yield.

Method 3. To an Et_2O (70 mL) solution of AlMe(BHT)$_2$ (4.00 g, 8.33 mmol) was added solid $SnCl_2$ (1.58 g, 8.33 mmol). The resulting solution was stirred for 72 h, during which time the solution turned from clear through yellow to red. Removal of solvent in vacuo, suspension in toluene, and filtration through Celite and a glass frit afforded pure product: yield 76%.

Method 4: as with method 3 but with AlEt(BHT)$_2$ (2.00 g, 4.05 mmol) and $SnCl_2$ (0.77 g, 4.06 mmol): yield 84%.

Method 5. To a pentane (65 mL) solution of AlMe(BHT)$_2$ (2.00 g, 4.17 mmol) was added $InCl_3$ (0.92 g, 4.16 mmol), and the resulting suspension was stirred rapidly for 5 h at room temperature. Et_2O (20 mL) was then added and the solution stirred for a further 12 h. The resulting precipitate was collected and dried in vacuo: yield ca. 60%.

Method 6: as with method 5, but with AlEt(BHT)$_2$ (0.50 g, 1.01 mmol) and $InCl_3$ (0.22 g, 0.99 mmol); yield 80%. Mp: 153–156 °C. IR: 3651 (w), 1290 (w), 1272 (sh), 1257 (m), 1201 (w), 1190 (w), 1150 (w), 1123 (w), 1089 (w), 1010 (w), 991 (w), 957 (w), 916 (m), 888 (m), 875 (m), 858 (w), 770 (m), 722 (m), 665 (w), 651 (w), 643 (w) cm^{-1}. ^1H NMR δ 7.17 (4 H, s, C_6H_2, BHT), 3.91 (4 H, q, *J*(H–H) = 7.1 Hz, OCH_2), 2.26 (6 H, s, CH_3, BHT), 1.52 (36 H, s, $C(CH_3)_3$, BHT), 0.62 (6 H, t, *J*(H–H) = 7.0 Hz, OCH_2CH_3). ^{13}C NMR: δ 153.85 (OC, BHT), 138.88 (*o*-C, BHT), 127.03 (*p*-C, BHT), 126.44 (*m*-C, BHT), 67.32 (OCH_2CH_3), 35.53 ($C(CH_3)_3$, BHT), 32.14 ($C(CH_3)_3$, BHT), 21.33 (CH_3, BHT), 11.15 (OCH_2CH_3). Mass spectrum: *m/z* 499 ($M^+ - Et_2O$). Anal. Calcd for $C_{34}H_{56}AlClO_3$: C, 70.99; H, 9.81. Found: C, 70.98; H, 9.84.

AlClMe(BHT)(OEt_2) (3). Method 1. To a pentane solution (50 mL) of $AlMe_2$(BHT)(OEt_2) (1.00 g, 2.86 mmol) was added Me_3SnCl (0.57 g, 2.86 mmol). The resulting solution was stirred for 3 h and then reduced to dryness under vacuum to give a white solid that was recrystallized from toluene–pentane: yield ca. 90%.

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(35) See for example: (a) Cyvin, S. J.; Klaeboe, P.; Rytter, E.; Øye, H. A. *J. Chem. Phys.* **1970**, *52*, 2776. (b) Gale, R. J.; Osteryoung, R. A. *Inorg. Chem.* **1980**, *19*, 2240. (c) Hvistendahl, J.; Klaeboe, P.; Rytter, E.; Øye, H. A. *Inorg. Chem.* **1984**, *23*, 706. (d) Dymek, C. J.; Wilkes, J. S.; Einarsrud, M.-A.; Øye, H. A. *Polyhedron* **1988**, *7*, 1139. (e) Wicelinski, S. P.; Gale, R. J.; Pamidimukkala, K. M.; Laine, R. A. *Anal. Chem.* **1988**, *60*, 2228.

(36) Leman, J. T.; Roman, H. A.; Barron, A. R. *J. Chem. Soc., Dalton Trans.*, in press.

Table V. Summary of X-ray Diffraction Data

compd	$AlCl_2(BHT)(OEt_2)$ (5)	$[Al(\mu\text{-}Cl)Me(BHT)]_2$ (6)	$[2,6\text{-}Me_2pyH][AlCl_2(BHT)_2]$ (9)
empir formula	$C_{19}H_{33}AlCl_2O_2$	$C_{32}H_{52}Al_2Cl_2O_2$	$C_{37}H_{56}AlCl_2O_2N$
cryst size, mm	0.43 × 0.47 × 0.50	0.11 × 0.45 × 0.50	0.23 × 0.33 × 0.37
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a, Å	10.796 (2)	10.410 (6)	9.3799 (8)
b, Å	17.753 (3)	9.865 (3)	13.898 (1)
c, Å	11.343 (2)	16.42 (1)	14.8255 (14)
α, deg			101.900 (8)
β, deg	97.36 (1)	97.20 (5)	91.080 (7)
γ, deg			98.050 (7)
V, $Å^3$	2156.0 (7)	1673 (1)	1870.3 (3)
Z	4	2	2
density (calcd), g cm^{-3}	1.206	1.178	1.145
abs coeff, mm^{-1}	0.349	0.272	0.225
radiation	Mo Kα (λ = 0.710 73 Å) graphite monochromator		
temp, K	173	195	193
2θ range, deg	4.0–50.0	4.0–45.0	4.0–45.0
index ranges	$0 \le h \le 12, 0 \le k \le 21, -13 \le l \le 13$	$0 \le h \le 11, 0 \le k \le 10, -17 \le l \le 17$	$0 \le h \le 10, -14 \le k \le 14, -15 \le l \le 15$
no. of rflns collected	3814	2537	5263
no. of index rflns	3617	2157	4598
no. of obsd rflns	3545 ($F > 1.0\sigma(F)$)	1715 ($F > 4.0\sigma(F)$)	4598 ($F > 0.0$)
weighting scheme	$w^{-1} = \sigma^2(\lvert F_o \rvert) + 0.0001(\lvert F_o \rvert)^2$	$w^{-1} = \sigma^2(\lvert F_o \rvert) + 0.0083(\lvert F_o \rvert)^2$	$w^{-1} = \sigma^2(\lvert F_o \rvert) + 0.0010(\lvert F_o \rvert)^2$
final R indexes	$R = 0.067, R_w = 0.078$	$R = 0.069, R_w = 0.088$	$R = 0.050, R_w = 0.062$
largest diff peak, e $Å^{-3}$	0.40	0.36	0.31

Method 2. To a suspension of $AlCl_3$ (4.90 g, 36.75 mmol) in pentane (70 mL) was added at room temperature via cannula $AlMe_3$ (36.75 mL, 2 M solution in hexane, 73.5 mmol). After the mixture was stirred for 12 h, the solvent was removed under vacuum at −6 °C and the residue trap-to-trap distilled. To the distillate was added pentane (30 mL) and BHT-H (23.73 g, 107.9 mmol) at ca. −20 °C. The resulting solution was warmed to room temperature. After 5 h copious quantities of white precipitate had deposited. This was allowed to settle, the solvent removed via cannula, and the solid washed with pentane (100 mL). Et_2O (40 mL) and pentane (40 mL) were then added, and the resulting suspension stirred overnight. The solvent was removed by filtration and the precipitate washed with additional pentane (2 × 30 mL): yield 77%. Mp: 102–104 °C. IR: 1423 (s), 1360 (m), 1354 (sh), 1265 (s), 1222 (m), 1201 (s), 1187 (m), 1157 (w), 1145 (m), 1125 (m), 1087 (s), 1021 (s), 993 (m), 954 (w), 887 (s), 881 (s), 866 (s), 834 (m), 791 (w), 775 (m), 766 (s), 722 (w), 682 (s), 672 (s), 659 (s), 622 (sh), 587 (m), 577 (m) cm^{-1}. ^1H NMR: δ 7.25 (2 H, s, C_6H_2, BHT), 3.52 (4 H, q, J(H–H) = 6.7 Hz, OCH_2), 2.31 (3 H, s, CH_3, BHT), 1.59 (18 H, s, $C(CH_3)_3$, BHT), 0.63 (6 H, t, J(H–H) = 7.1 Hz, OCH_2CH_3), −0.15 (3 H, s, Al–CH_3). ^{13}C NMR: δ 153.81 (0C, BHT), 139.06 (o-C, BHT), 126.89 (m-C, BHT), 126.30 (p-C, BHT), 67.32 (OCH_2CH_3), 35.14 ($C(CH_3)_3$, BHT), 31.36 ($C(CH_3)_3$, BHT), 21.35 (CH_3, BHT), 12.53 (OCH_2CH_3), −5.76 (Al–CH_3). Mass spectrum (CI): m/z 370 (M^+, 51%). Anal. Calcd for $C_{20}H_{36}AlClO_2$: C, 64.75; H, 9.78. Found: C, 64.78; H, 9.99.

$AlClEt(BHT)(OEt_2)$ (4). To a Schlenk flask charged with $AlEt_2(BHT)(OEt_2)$ (1.00 g, 2.65 mmol) was added consecutively pentane (30 mL), ether (10 mL), and $SnMe_3Cl$ (0.53 g, 2.66 mmol). The resulting solution was stirred for 12 h. Removal of all volatiles in vacuo led to the isolation of a white solid: yield ca. 90%. Mp: 78–80 °C. IR: 3651 (m), 1294 (sh), 1273 (s), 1266 (sh), 1232 (m), 1202 (m), 1193 (m), 1153 (m), 1123 (w), 1089 (m), 1017 (s), 994 (m), 956 (w), 922 (w), 904 (s), 888 (m), 860 (m), 838 (w), 796 (w), 772 (s), 722 (m), 639 (m), 606 (m), 586 (m) cm^{-1}. ^1H NMR: δ 7.23 (2 H, s, C_6H_2, BHT), 3.55 (4 H, q, J(H–H) = 7.1 Hz, o-CH_2), 2.30 (3 H, s, CH_3, BHT), 1.58 (18 H, s, $C(CH_3)_3$, BHT), 1.37 (3 H, t, J(H–H) = 8.1 Hz, $AlCH_2CH_3$), 0.66 (6 H, t, J(H–H) = 7.1 Hz, OCH_2CH_3), 0.41 (2 H, m, $AlCH_2CH_3$). ^{13}C NMR: δ 153.93 (OC, BHT), 139.04 (o-C, BHT), 126.87 (m-C, BHT), 126.30 (p-C, BHT), 67.43 (OCH_2), 35.16 ($C(CH_3)_3$, BHT), 31.40 ($C(CH_3)_3$, BHT), 21.33 (CH_3, BHT), 12.54 (OCH_2CH_3), 9.40 ($AlCH_2CH_3$), 3.55 ($AlCH_2CH_3$). Mass spectrum: m/z 178 ($M^+ - Et_2O$). Anal. Calcd for $C_{21}H_{38}AlClO_2$: C, 65.52; H, 9.95. Found: C, 63.46; H, 9.55.

$AlCl_2(BHT)(OEt_2)$ (5). Method 1. To a solution of $AlMe_2(BHT)(OEt_2)$ (2.06 g, 5.71 mmol) in pentane (40 mL) was added solid Me_3SnCl (2.30 g, 11.5 mmol). After the mixture was stirred, (3 h), the volatiles were removed under vacuum to yield a white crystalline solid: yield ca. 90%.

Method 2: As for method 1, but with $AlEt_2(BHT)(OEt_2)$ (2.00 g, 5.29 mmol) and Me_3SnCl (2.11 g, 10.6 mmol); yield ca. 90%.

Method 3. $AlClMe(BHT)(OEt_2)$ (1.00 g, 2.70 mmol) was dissolved in a mixture of pentane (30 mL) and Et_2O (10 mL). To this solution was added Me_3SnCl (0.54 g, 2.71 mmol). Removal of volatiles after 12 h of stirring leads to the isolation of white solid: yield ca. 90%.

Method 4. To $AlMe(BHT)_2$ (2.00 g, 4.17 mmol) and $AlCl_3$ (0.56 g, 4.20 mmol) was added Et_2O (30 mL). The resulting yellow solution was stirred for 12 h at room temperature. Removal of all volatiles and subsequent recrystallization from CH_2Cl_2 yielded X-ray-quality crystals: yield 86%. Mp: 112–117 °C. IR: 3651 (w), 1288 (sh), 1264 (s), 1221 (w), 1202 (w), 1125 (w), 1067 (m), 1007 (m), 990 (m), 904 (m), 887 (m), 872 (m), 866 (m), 773 (m), 767 (m), 723 (w), 636 (m), 566 (m) cm^{-1}. ^1H NMR: δ 7.22 (2 H, s, C_6H_2, BHT), 3.63 (4 H, q, J(H–H) = 6.8 Hz, OCH_2CH_3), 2.27 (3 H, s, BHT), 1.59 (18 H, s, $C(CH_3)_3$, BHT), 0.66 (6 H, t, J(H–H) = 7.0 Hz, OCH_2CH_3). ^{13}C NMR: δ 152.75 (OC, BHT), 139.34 (o-C, BHT), 126.45 (m-C, BHT), 126.32 (p-C, BHT), 69.34 (OCH_2CH_3, ether), 35.10 ($C(CH_3)_3$, BHT), 31.52 ($C(CH_3)_3$, BHT), 21.31 (CH_3, BHT), 12.46 (OCH_2CH_3, ether). Mass spectrum: m/z 389 (M^+), 315 ($M^+ - Et_2O$). Anal. Calcd for $C_{19}H_{33}AlCl_2O_2$: C, 58.31; H, 8.50. Found: C, 58.21; H, 8.70.

$[Al(\mu\text{-}Cl)Me(BHT)]_2$ (6). To a pentane solution (50 mL) of $AlMe(BHT)_2$ (3.00 g, 6.25 mmol) was added BCl_3 (6.25 mL, 6.25 mmol) via cannula. The resulting solution was stirred for 12 h, after which the volatiles were removed in vacuo. ^1H NMR spectroscopy of the crude reaction mixture revealed the presence of two types of BHT ligands in a 1:1 ratio. Fractional crystallization from pentane–benzene yielded X-ray-quality crystals of the aluminum-containing product: yield ca. 70%. (The boron side product $BCl_2(BHT)$ was isolated as an impure yellow oil.) Mp: 179–189 °C. IR: 1290 (sh), 1258 (s), 1203 (m), 1122 (m), 1074 (w), 1015 (w), 955 (m), 916 (s), 884 (w), 861 (m), 815 (w), 781 (w), 767 (m), 718 (m), 692 (sh), 674 (s), 593 (m) cm^{-1}. ^1H NMR: δ 7.16 (4 H, s, C_6H_2, BHT), 2.28 (6 H, s, CH_3, BHT), 1.49 (36 H, s, $C(CH_3)_3$, BHT), −0.04 (6 H, s, $AlCH_3$). ^{13}C NMR: δ 152.19 (OC, BHT), 138.66 (o-C, BHT), 126.32 (m-C, BHT), 126.22 (p-C, BHT), 34.69 ($C(CH_3)_3$, BHT), 31.30 ($C(CH_3)_3$, BHT), 21.33 (CH_3, BHT), −5.67 ($AlCH_3$). Anal. Calcd for $C_{32}H_{52}Al_2Cl_2O_2$: C, 64.74; H, 8.83. Found: C, 64.45; H, 8.68.

$O{=}CC(^tBu){=}C(H)C(Me)(CH_2Cl)C(H){=}C(^tBu)$ (7). A Schlenk flask was charged with $AlMe(BHT)_2$ (10.0 g, 20.8 mmol) and $AlCl_3$ (3.7 g, 27.8 mmol). To this was added CH_2Cl_2 (50 mL), and the resulting solution was stirred at room temperature for 12 h. During this time, the reaction mixture turns from pale yellow

Table VI. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Thermal Parameters ($\times10^4$ Å^2) for the Non-Hydrogen Atoms in $\mathrm{AlCl_2(BHT)(OEt_2)}$ (5)

	x	*y*	*z*	*U*(eq)[a]
Al(1)	259 (1)	8075 (1)	4282 (1)	209 (3)
Cl(1)	−172 (1)	6916 (1)	4155 (1)	440 (4)
Cl(2)	1933 (1)	8298 (1)	3581 (1)	527 (4)
O(1)	−956 (2)	8668 (1)	3870 (2)	196 (8)
O(2)	718 (2)	8286 (1)	5897 (2)	198 (8)
C(1)	−2119 (3)	8850 (2)	3320 (3)	162 (10)
C(2)	−3130 (3)	8900 (2)	4011 (3)	179 (11)
C(3)	−4300 (3)	9107 (2)	3417 (3)	211 (11)
C(4)	−4497 (3)	9274 (2)	2213 (3)	215 (11)
C(5)	−3494 (3)	9227 (2)	1584 (3)	218 (11)
C(6)	−2302 (3)	9010 (2)	2087 (3)	176 (11)
C(7)	−2990 (3)	8766 (2)	5363 (3)	209 (11)
C(8)	−2098 (4)	9356 (2)	5980 (3)	282 (13)
C(9)	−4240 (3)	8850 (2)	5873 (3)	311 (13)
C(10)	−2551 (3)	7958 (2)	5676 (3)	249 (12)
C(11)	−5776 (4)	9506 (3)	1622 (3)	358 (14)
C(12)	−1251 (3)	8948 (2)	1295 (3)	216 (11)
C(13)	−814 (3)	8121 (2)	1244 (3)	255 (12)
C(14)	−167 (3)	9478 (2)	1725 (3)	287 (13)
C(15)	−1695 (4)	9171 (2)	2 (3)	328 (14)
C(16)	831 (4)	7728 (2)	6868 (3)	282 (13)
C(17)	309 (4)	8015 (2)	7951 (3)	373 (15)
C(18)	1274 (3)	9027 (2)	6202 (3)	257 (12)
C(19)	2639 (4)	8983 (3)	6640 (4)	407 (15)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VII. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Thermal Parameters ($\times10^3$ Å^2) for the Non-Hydrogen Atoms in $[\mathrm{Al(\mu\text{-}Cl)Me(BHT)}]_2$ (6)

	x	*y*	*z*	*U*(eq)[a]
Al(1)	−368 (2)	651 (2)	851 (1)	39 (1)
Cl(1)	1431 (1)	613 (2)	193 (1)	57 (1)
O(1)	−930 (3)	2239 (3)	780 (2)	29 (1)
C(1)	−1458 (4)	3380 (5)	1074 (3)	24 (2)
C(2)	−656 (4)	4413 (4)	1418 (3)	24 (2)
C(3)	−1242 (5)	5595 (5)	1676 (3)	34 (2)
C(4)	−2588 (4)	5768 (5)	1576 (3)	30 (2)
C(5)	−3342 (4)	4721 (5)	1240 (3)	28 (2)
C(6)	−2836 (4)	3520 (5)	949 (3)	30 (2)
C(7)	837 (5)	4330 (5)	1530 (3)	30 (2)
C(8)	1328 (5)	4201 (6)	691 (4)	43 (2)
C(9)	1472 (5)	5593 (5)	1932 (4)	44 (2)
C(10)	1317 (5)	3117 (6)	2081 (4)	41 (2)
C(11)	−3172 (5)	7070 (6)	1827 (4)	42 (2)
C(12)	−3735 (4)	2425 (5)	552 (3)	29 (2)
C(13)	−3606 (5)	1069 (5)	1018 (4)	39 (2)
C(14)	−5191 (5)	2810 (6)	535 (4)	41 (2)
C(15)	−3498 (5)	2267 (6)	−353 (3)	40 (2)
C(16)	−97 (6)	−471 (6)	1813 (5)	59 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VIII. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Thermal Parameters ($\times10^3$ Å^2) for the Non-Hydrogen Atoms in $[\mathrm{2,6\text{-}Me_2pyH}][\mathrm{AlCl_2(BHT)_2}]$ (9)

	x	*y*	*z*	*U*(eq)[a]
Al(1)	2213 (1)	7336 (1)	3552 (1)	239 (3)
Cl(1)	806 (1)	7850 (1)	4658 (1)	345 (3)
Cl(2)	4255 (1)	7569 (1)	4329 (1)	355 (3)
O(1)	1519 (2)	6124 (1)	3128 (1)	257 (7)
O(2)	2432 (2)	8101 (1)	2785 (1)	253 (6)
C(1)	1138 (3)	5196 (2)	2605 (2)	216 (9)
C(2)	1911 (3)	4414 (2)	2720 (2)	261 (10)
C(3)	1619 (3)	3519 (2)	2073 (2)	314 (11)
C(4)	592 (3)	3342 (2)	1358 (2)	322 (11)
C(5)	−259 (3)	4075 (2)	1326 (2)	270 (10)
C(6)	−50 (3)	4999 (2)	1947 (2)	238 (9)
C(7)	3049 (3)	4516 (2)	3510 (2)	341 (11)
C(8)	2512 (3)	5010 (2)	4443 (2)	394 (12)
C(9)	4460 (3)	5101 (3)	3279 (2)	452 (13)
C(10)	3379 (4)	3493 (3)	3638 (3)	526 (14)
C(11)	356 (4)	2368 (2)	658 (2)	489 (13)
C(12)	−1133 (3)	5728 (2)	1909 (2)	273 (10)
C(13)	−451 (3)	6601 (2)	1502 (2)	344 (11)
C(14)	−1684 (3)	6084 (2)	2874 (2)	348 (11)
C(15)	−2466 (3)	5236 (2)	1280 (2)	421 (12)
C(16)	2461 (3)	8578 (2)	2069 (2)	213 (9)
C(17)	1697 (3)	9403 (2)	2118 (2)	244 (9)
C(18)	1708 (3)	9853 (2)	1358 (2)	282 (10)
C(19)	2453 (3)	9552 (2)	578 (2)	293 (10)
C(20)	3243 (3)	8785 (2)	576 (2)	283 (10)
C(21)	3288 (3)	8279 (2)	1291 (2)	234 (9)
C(22)	869 (3)	9821 (2)	2963 (2)	311 (10)
C(23)	−450 (3)	9065 (2)	3062 (2)	384 (11)
C(24)	286 (4)	10680 (2)	2870 (2)	475 (13)
C(25)	1874 (3)	10111 (2)	3846 (2)	374 (11)
C(26)	2406 (4)	10038 (2)	−244 (2)	448 (13)
C(27)	4285 (3)	7475 (2)	1234 (2)	270 (10)
C(28)	3445 (3)	6461 (2)	1290 (2)	381 (11)
C(29)	5479 (3)	7824 (2)	2000 (2)	391 (11)
C(30)	5038 (3)	7296 (2)	310 (2)	397 (12)
N(1)	2976 (2)	8234 (2)	6465 (2)	284 (8)
C(31)	2709 (3)	7517 (2)	6954 (2)	328 (11)
C(32)	3485 (4)	7642 (2)	7773 (2)	419 (12)
C(33)	4510 (3)	8470 (3)	8057 (2)	435 (12)
C(34)	4726 (3)	9191 (2)	7537 (2)	366 (11)
C(35)	3940 (3)	9071 (2)	6723 (2)	292 (10)
C(36)	1583 (4)	6651 (2)	6566 (2)	532 (14)
C(37)	4062 (4)	9786 (2)	6099 (2)	415 (12)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

to dark brown. Removal of all volatiles under vacuum leaves a glassy solid. Hydrolysis with $\mathrm{H_2O}$–HCl followed by extraction with $\mathrm{Et_2O}$ leads to a white solid, which may be further purified by either sublimation or crystallization (pentane): yield (after double sublimation) 36%. Mp: 67–70 °C. IR: 1663 (s), 1646 (s), 1631 (sh), 1618 (sh), 1321 (m), 1274 (m), 1259 (sh), 1249 (m), 1202 (w), 1166 (m), 1141 (w), 1083 (w), 1021 (w), 973 (w), 942 (m), 932 (m), 910 (m), 894 (m), 879 (m), 816 (w), 779 (w), 735 (s), 723 (m) $\mathrm{cm^{-1}}$. ^{1}H NMR: δ 6.25 (2 H, s, $\mathrm{C_6}H_2$), 2.88 (2 H, S, $\mathrm{C}H_2\mathrm{Cl}$), 1.35 (18 H, s, $\mathrm{C(C}H_3)_3$), 0.83 (3 H, s, $\mathrm{C}H_3$). ^{13}C NMR: δ 185.69 (O*C*), 148.44 (*m*-*C*), 142.48 (*o*-*C*), 52.18 ($C\mathrm{H_2Cl}$), 40.44 (*p*-*C*), 35.15 ($C\mathrm{(CH_3)_3}$), 29.62 ($\mathrm{C(}C\mathrm{H_3)_3}$), 23.70 ($C\mathrm{H_3}$). Mass spectrum: *m*/*z* 268 ($\mathrm{M^+}$). Anal. Calcd for $\mathrm{C_{16}H_{25}ClO}$: C, 71.49; H, 9.38. Found: C, 72.12; H, 9.20.

O=CC(^{t}Bu)=C(H)C(Me)($\mathrm{CD_2Cl}$)C(H)=C(^{t}Bu) (7-*d*$_2$). The same procedure was followed as above, with the substitution of $\mathrm{CD_2Cl_2}$ for $\mathrm{CH_2Cl_2}$. ^{1}H NMR: δ 6.25 (2 H, s, $\mathrm{C_6}H_2$), 1.35 (18 H, s, $\mathrm{C(C}H_3)_3$), 0.84 (3 H, s, $\mathrm{C}H_3$). ^{13}C NMR: δ 185.70 (*o*-*C*), 148.46 (*m*-*C*), 142.36 (*o*-*C*), 51.40 (quintet, $C\mathrm{D_2Cl}$, *J*(C–D) = 22.89 Hz), 40.28 (*p*-*C*), 35.14 ($C\mathrm{(CH_3)_3}$), 29.63 ($\mathrm{C(}C\mathrm{H_3)_3}$), 23.68 ($\mathrm{CH_3}$).

Reaction of $\mathrm{AlClMe(BHT)(OEt_2)}$ with $\mathrm{AlCl_3}$ in $\mathrm{CH_2Cl_2}$. To $\mathrm{AlClMe(BHT)(OEt_2)}$ (2.0 g, 5.40 mmol) and $\mathrm{AlCl_3}$ (0.72 g, 5.40 mmol) was added $\mathrm{CH_2Cl_2}$ (40 mL). The resulting mixture was stirred for 12 h at room temperature. Hydrolysis with HCl–$\mathrm{H_2O}$ and extraction with $\mathrm{Et_2O}$ afforded a mixture of 7 (90%) and BHT-H (10%) as determined by ^{1}H NMR spectroscopy.

Kinetics Studies. $\mathrm{AlMe(BHT)_2}$ and $\mathrm{AlCl_3}$ were added together in various ratios in $\mathrm{CH_2Cl_2}$ (50 mL). The reaction mixture was stirred at room temperature, and 1-mL aliquots were removed at timed intervals. The aliquots were quenched with aqueous acid (1.0 M HCl) and extracted with pentane. The ratio of BHT-H to 7 was determined by gas chromatography, by comparison with standard solutions. Selected experimental details and calculated first-order rate constants are given in Table III.

$\mathrm{AlCl(BHT)_2(NCMe)}$ (8). To $\mathrm{AlMe(BHT)_2}$ (3.0 g, 6.24 mmol) and $\mathrm{InCl_3}$ (1.38 g, 6.24 mmol) was added at room temperature MeCN (30 mL). The resulting suspension was briefly heated with a heat gun to dissolve all solids. The solution was stirred at room temperature overnight. Removal of volatiles in vacuo gave a white solid: yield >90%. Mp: 131–133 °C. IR: 2312 (m), 2282 (m), 1258 (m), 1234 (s), 1216 (m), 1121 (w), 954 (w), 919 (w), 895 (s), 869 (m), 857 (m), 776 (m), 751 (sh), 722 (m), 673 (m), 665 (w), 612 (m) $\mathrm{cm^{-1}}$. ^{1}H NMR: δ 7.24 (4 H, s, $\mathrm{C_6}H_2$), 2.30 (6 H, s, $\mathrm{C}H_3$), 1.66 (36 H, s, $\mathrm{C(C}H_3)_3$), 0.23 (3 H, s, $\mathrm{NCC}H_3$). ^{13}C NMR: δ 153.18 (O*C*, BHT), 139.05 (*o*-*C*, BHT), 127.11 (*m*-*C*, BHT), 126.53 (*p*-*C*,

BHT), 35.32 ($C(\mathrm{CH_3})_3$, BHT), 32.15 ($\mathrm{C}(C\mathrm{H_3})_3$, BHT), 21.33, ($C\mathrm{H_3}$, BHT), −0.84 ($\mathrm{NC}C\mathrm{H_3}$). Mass spectrum: *m/z* 500 ($\mathrm{M^+}$ − MeCN).

Reaction of $\mathbf{AlMe(BHT)_2}$ with $\mathbf{ZnCl_2}$. A mixture of $\mathrm{AlMe(BHT)_2}$ (3.00 g, 6.25 mmol) and $\mathrm{ZnCl_2}$ (2.55 g, 18.71 mmol) was refluxed in $\mathrm{Et_2O}$ (50 mL) for 12 h. Removal of the solvent under vacuum gave a white solid, which from ^{1}H NMR spectroscopy was analyzed as $\mathrm{AlMe(BHT)_2(OEt_2)}$ (22%) and $\mathrm{AlCl(BHT)_2(OEt_2)}$ (78%).

$\mathbf{[2,6\text{-}Me_2pyH][AlCl_2(BHT)_2]}$ (9). To a solution of $\mathrm{AlMe(BHT)_2}$ (2.0 g, 4.2 mmol) in $\mathrm{Et_2O}$ (30 mL) was added 2,6-$\mathrm{Me_2pyHCl}$ (1.2 g, 8.4 mmol). The resulting solution was stirred for 48 h, during which time a white precipitate was formed. The solvent was removed by cannula, and the precipitate was then washed with pentane (30 mL) and dried in vacuo. Structure-quality crystals were grown from methylene chloride: yield ca. 30%. Mp: 183–185 °C. IR: 3270 (m), 3195 (m), 3151 (m), 1634 (s), 1240 (s), 1218 (s), 1203 (m), 1171 (m), 1122 (w), 1029 (w), 881 (s), 863 (s), 790 (sh), 780 (s), 721 (m), 665 (m), 647 (m), 605 (m) $\mathrm{cm^{-1}}$. ^{1}H NMR: δ 12.89 (1 H, s, N*H*, lut), 7.26 (4 H, s, $\mathrm{C_6}H_2$, BHT), 6.58 (1 H, t, *J*(H–H) = 7.9 Hz, *p-H*, lut), 5.95 (2 H, t, *J*(H–H) = 7.9 Hz, *m-H*, lut), 2.31 (6 H, s, $\mathrm{C}H_3$, BHT), 2.09 (6 H, s, $\mathrm{C}H_3$, lut), 1.82 (36 H, s, $\mathrm{C(C}H_3)_3$, BHT). ^{13}C NMR: δ 154.69 (O*C*, BHT), 144.68 (*o-C*, lut), 139.52 (*o-C*, BHT), 128.29 (*m-C*, lut), 126.32 (*m-C*, BHT), 125.55 (*p-C*, BHT), 123.82 (*p-C*, lut), 35.69 ($C(\mathrm{CH_3})_3$, BHT), 32.70 ($\mathrm{C}(C\mathrm{H_3})_3$, BHT), 21.41 ($C\mathrm{H_3}$, BHT), 19.65 ($C\mathrm{H_3}$, lut). Mass spectrum: *m/z* 500 ($\mathrm{M^+}$ − 2,6-$\mathrm{Me_2pyHCl}$). Anal. Calcd for $\mathrm{C_{37}H_{56}AlCl_2NO_2}$: C, 68.92; H, 8.76; N, 2.17. Found: C, 66.91; H, 8.53; N, 2.27.

X-ray Crystallographic Studies. A crystal data summary is given in Table V; fractional atomic coordinates are listed in Tables VI–VIII.

X-ray data for compounds 5 and 9 were collected on a Siemens P3 diffractometer equipped with a modified LT-2 low-temperature system and a P21 diffractometer with an LT-1 low-temperature system, respectively. Laue symmetry, crystal class, unit-cell-parameter, and crystal orientation matrix determinations were carried out by previously described techniques.[16b,h,37] All crystallographic calculations were carried out using either the UCI-modified version of the UCLA Crystallographic Computer Package[38] or the SHELXTL-PLUS program set.[39] The analytical scattering factors for neutral atoms were used through the analysis;[40] the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included.

The structure was solved by direct methods and refined by full least-squares methods (SHELXTL-PLUS). Hydrogen atoms were included using a riding model with *d*(C–H) = 0.96 Å and *U*(iso) = 0.08 Å^2. Refinement of positional and anisotropic thermal parameters led to convergence (see Table V).

A crystal of compound 6 was mounted directly onto a fiber which was mounted on the goniometer via a glass pin with silicone grease. Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[16a] using a Nicolet R3m/v diffractometer operating in the θ–2θ scan mode. Data collection was controlled by using the Nicolet P3 program.[41] Empirical absorption corrections were applied to the data using the program PSICOR. Further experimental data are given in Table V.

The structure was solved using the direct-methods program XS, which revealed the positions of most of the heavy atoms. Most but not all of the hydrogens were visible in the final difference map. Hydrogens were included as fixed-atom contributors in the final cycles: *d*(C–H) = 0.96 Å and *U*(iso) = 0.08 Å^2. Details of the refinement are given in Table V. Atomic scattering factors and anomalous scattering parameters were as given in ref 40.

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Supplementary Material Available: Listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for 5–7 and 9 and a listing of positional and isotropic thermal parameters for 7 (19 pages). Ordering information is given on any current masthead page.

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