squares refinement gave an R value of 0.025 (R_w = 0.035) for 3469 data with $I > 3\sigma(I)$. The final Fourier difference map showed no peaks greater than ±0.49 e/Å^3.

[(η^5-C_5Me_5)Mo(CO)$_3$(CF_2)]SO_3CF_3 (4). An orange prism of 4 measuring 0.36 × 0.56 × 0.94 mm was obtained by slow cooling of a CH_2Cl_2 solution to -55 °C. Mounting in a glass capillary under nitrogen and cooling to -100 °C for alignment and data collection was carried out quickly in order to minimize decay of the thermally sensitive compound. Random centering on 48 strong reflections (22° ≤ 2θ ≤ 30°) suggested a tetragonal unit cell; 4/*mmm* Laue symmetry was confirmed by examination of $\pm h,\pm k,\pm l$ and $\pm k,\pm h,\pm l$ equivalent reflections. A total of 5823 redundant data were collected with use of a variable ω scan rate of 6.0–30.0° min^{-1} with indices $\pm h,\pm k,\pm l$, giving 1420 unique reflections (R_{int} = 0.016). Three standard reflections monitored after every 100 data collected showed no systematic variation. The data were corrected for absorption by using the semiempirical φ-scan method. Systematic absences were consistent with either $P4_2/mbc$ or $P4_2bc$. A direct-methods solution in $P4_2/mbc$ followed by a series of difference Fourier maps placed all non-hydrogen atoms. Although full anisotropic refinement in $P4_2bc$ with all hydrogen atoms placed in idealized positions gave a low final R value of 0.034, the η^5-C_5Me_5 ring and the C(3)–O(3) carbonyl group were highly distorted. In the alternative centrosymmetric space group $P4_2/mbc$, a crystallographically imposed mirror plane bisects both the molybdenum complex and the triflate counteranion and requires disorder between the difluorocarbene and the C(3)–O(3) carbonyl ligands. Nevertheless, full refinement in this space group yielded a structure with no significant distortions and indicated that $P4_2/mbc$ was the correct choice. Due to moderate correlation between the anisotropic thermal coefficients of F(2) and O(3), both C(3) and O(3) were made isotropic for the final stages of refinement, which gave a final R value of 0.039 by use of 1252 reflections with $I > 3\sigma(I)$. The final Fourier difference map revealed a residual peak of 1.13 e/Å^3 associated with the triflate counteranion, with no other peak greater than 0.51 e/Å^3.

Acknowledgment. This work has been supported by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the NSF EPSCoR program (Grant No. RII-8610680). We would like to thank Drs. J. Korp and B. Santarsiero for valuable assistance and discussions concerning the crystallography of 4.

Supplementary Material Available: Tables of complete data collection parameters (Tables S1 and S5), bond angles (Tables S2 and S6), anisotropic thermal parameters (Tables S3 and S7), and hydrogen atom coordinates and isotropic thermal parameters (Tables S4 and S8) (13 pages); listings of calculated and observed structure factors (Tables S9 and S10) (20 pages). Ordering information is given on any current masthead page.

Sterically Crowded Aryloxide Compounds of Aluminum: Electronic and Steric Effects

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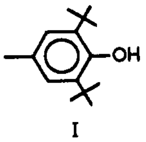
The mononuclear, four-coordinate aluminum compounds AlR_2(BHT)L and AlR$(BHT)_2$L [R = Me, Et; BHT = 2,6-di-*tert*-butyl-4-methylphenoxide; L = 2-Mepy, 4-Mepy, 2,6-Me_2py, CH_3CN, $N(C_2H_4)_3CH$, $HNEt_2$, HN^iBu_2, H_2N^tBu, H_2N^nBu, NH_3, py·O] are obtained when AlR_3 is treated with the correct molar equivalent of BHT–H and the appropriate Lewis base. The aluminum–methyl ^{13}C NMR chemical shift for the monoaryloxide compounds $AlMe_2$(BHT)L is dependent primarily on the steric bulk of the Lewis base. The reaction of $AlMe_3$ with pentafluorophenol yields $[Me_2Al(\mu\text{-}OC_6F_5)]_2$. Cleavage of the phenoxide-bridged dimer by $N(C_2H_4)_3CH$ leads to the formation of the Lewis acid–base complex. The molecular structures of $AlMe_2$(BHT)(2,6-Me_2py) (**4**), $AlEt_2$(BHT)(H_2N^tBu) (**16**), $AlEt_2$(BHT)(py·O) (**19**), AlMe$(BHT)_2$(py·O)·$^1/_2CH_2Cl_2$ (**20**), and $AlMe_2(OC_6F_5)[N(C_2H_4)_3CH]$ (**23**) have been determined by X-ray crystallography. The relationship between Al–O bond distances, Al–O–C bond angles, and the presence of Al–O π-bonding is discussed. Crystal data for **4**: monoclinic, $P2_1/n$, a = 9.994 (2) Å, b = 21.647 (4) Å, c = 10.822 (2) Å, β = 93.74 (2)° (198 K), Z = 4, R = 0.058, R_w = 0.066. Crystal data for **16**: monoclinic, $P2_1/n$, a = 9.025 (2) Å, b = 13.862 (2) Å, c = 19.339 (4) Å, β = 96.60 (1)° (183 K), Z = 4, R = 0.060, R_w = 0.068. Crystal data for **19**: monoclinic, $P2_1/n$, a = 9.630 (2) Å, b = 18.232 (4) Å, c = 13.980 (3) Å, β = 101.62 (2)° (173 K), Z = 4, R = 0.055, R_w = 0.055. Crystal data for **20**: monoclinic, $C2/c$, a = 25.025 (4) Å, b = 16.877 (3) Å, c = 19.261 (5) Å, β = 117.59 (2)° (193 K), Z = 8, R = 0.073, R_w = 0.077. Crystal data for **23**: triclinic, $P\bar{1}$, a = 6.9822 (6) Å, b = 9.4896 (8) Å, c = 12.7230 (9) Å, α = 93.140 (6)°, β = 94.650 (6)°, = 102.580 (7)° (183 K), Z = 2, R = 0.039, R_w = 0.044.

Introduction

Recent work in our laboratories has been concerned with the synthesis and characterization of aluminum aryloxide compounds derived from 2,6-di-*tert*-butyl-4-methylphenol (I) (BHT–H from the trivial name butylated hydroxytoluene).[2-4] The use of this sterically hindered aryloxide ligand allows for the isolation of monomeric four-coordi-



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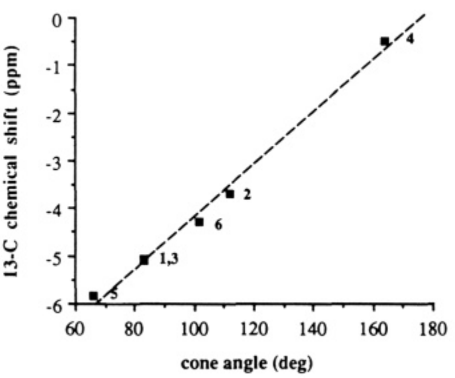
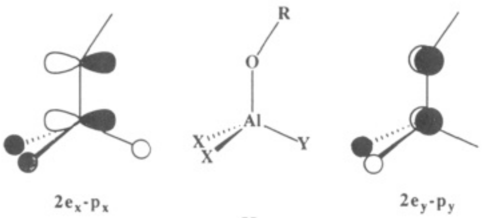


Figure 1. Aluminum–methyl ^{13}C NMR shift (δ) as a function of nitrogen donor ligand cone angle (θ). The numbering of the points corresponds to the text.

nate compounds, $AlX_2Y(BHT)$. We have attributed the presence of unusually short Al–O bond distances (1.70–1.74 Å) and large Al–O–C bond angles (140–164°) to π-type interactions between the oxygen lone pairs and the two π-acceptor orbitals $2e_x$ and $2e_y$ of the AlX_2Y moiety (II)



II

which are Al–X and Al–Y σ^*-antibonding.[2] Our synthetic,[3] spectroscopic,[5] and theoretical[6] studies indicate that such an interaction is retained even with the use of less sterically hindered aryloxides. In addition, ab initio calculations[6] suggest that the presence of electron-withdrawing groups on the phenyl ring should result in a decrease of π-donation from oxygen to aluminum.

We report here the synthesis and structural characterization of a series of monomeric, four-coordinate aluminum aryloxide compounds $AlMe_{3-x}(OR)_xL$ ($x = 1, 2$). The structures of the compounds are discussed in terms of the steric bulk of the Lewis base and the presence of π-bonding between oxygen and the four-coordinate aluminum center.

Results and Discussion

Complexes of $AlMe_2(BHT)$ with Nitrogen Donor Ligands. The addition of 1 equiv of a nitrogen donor Lewis base (L) to $AlMe_2(BHT)(OEt_2)$[4] in pentane results, after the removal of all volatiles, in the quantitative formation of the Lewis acid–base complex $AlMe_2(BHT)L$ (eq 1). If an equimolar mixture of $AlMe_3$ and BHT–H is

$$AlMe_2(BHT)(OEt_2) + L \rightarrow AlMe_2(BHT)L \quad (1)$$

$$AlMe_3 + BHT\text{–}H \rightarrow \text{“}AlMe_2(BHT)\text{”} \xrightarrow{L} AlMe_2(BHT)L + Me_3AlL + AlMe(BHT)_2L \quad (2)$$

L = py (**1**), 2-Mepy (**2**), 4-Mepy (**3**), 2,6-Me_2py (**4**), CH_3CN (**5**), $N(C_2H_4)_3CH$ (**6**)

employed in place of $AlMe_2(BHT)(OEt_2)$, Me_3AlL and $AlMe(BHT)_2L$ are formed as minor coproducts, due to the multispecies equilibrium of $AlMe_2(BHT)$ in hydrocarbon solution.[7]

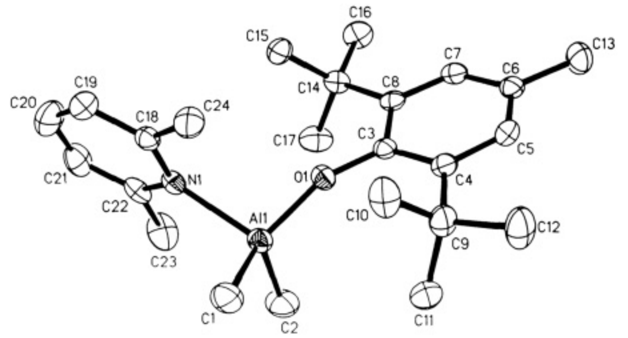


Figure 2. Structure of $AlMe_2(BHT)(2,6\text{-}Me_2py)$ (**4**). Thermal ellipsoids are drawn at the 40% level, and hydrogen atoms are omitted for clarity.

Table I. Selected Bond Length (Å) and Bond Angles (deg) in $AlMe_2(BHT)(py)$[a] (1) and $AlMe_2(BHT)(2,6\text{-}Me_2py)$ (4)

	$AlMe_2(BHT)py$	$AlMe_2(BHT)$-$(2,6\text{-}Me_2py)$
Al(1)–O(1)	1.740 (4)	1.744 (2)
Al(1)–N(1)	1.993 (5)	2.074 (2)
Al(1)–C(1)	1.964 (6)	1.971 (3)
Al(1)–C(2)	1.956 (6)	1.965 (3)
O(1)–C(3)	1.357 (5)	1.358 (3)
O(1)–Al(1)–N(1)	101.3 (2)	102.1 (1)
O(1)–Al(1)–C(1)	116.8 (2)	119.7 (1)
O(1)–Al(1)–C(2)	115.5 (2)	112.5 (1)
N(1)–Al(1)–C(1)	100.0 (2)	99.7 (1)
N(1)–Al(1)–C(2)	105.9 (2)	115.7 (1)
C(1)–Al(1)–C(2)	114.3 (3)	106.8 (2)
Al(1)–O(1)–C(3)	156.1 (3)	158.0 (2)

[a] See ref 3.

We have shown previously[8] that the ^{13}C NMR shift of the aluminum–methyl carbons in Me_3AlPR_3 complexes is largely dependent on the steric bulk of the phosphine ligand, as measured by the cone angle (θ). Bulkier phosphines force the aluminum coordination sphere to become more distorted from planarity, and the increased p character in the Al–C bond is apparent in the downfield shift of the Al–CH_3 carbon resonance. A similar dependence of the aluminum–methyl ^{13}C NMR shift on the steric bulk of the Lewis base is found for **1**–**6**; that is, the greater the steric bulk of the Lewis base, the more downfield the shift of the methyl resonance (see Figure 1).

We have calculated the cone angles for the nitrogen donor Lewis bases coordinated to aluminum in an analogous manner to that of Tolman for tertiary phosphines.[9] The aluminum–nitrogen bond length was assumed to be constant at 1.98 Å.[10]

The increased distortion from planarity of the aluminum coordination in Me_3AlPR_3 with increased phosphine steric bulk has been confirmed by X-ray crystallography.[11] In order to confirm that a similar structural distortion is observed for the aryloxide complexes with non-phosphine Lewis bases, we have determined the crystal structure of **4** (Figure 2). Selected bond lengths and angles for **4** are

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

(2) Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* **1988**, *7*, 2543.

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given in Table I, along with the corresponding values for $\mathrm{AlMe_2(BHT)py}$ (1).[3] A comparison of the sum of the interligand angles not associated with the py or 2,6-$\mathrm{Me_2py}$ nitrogens [346.6° (1) and 339.0° (4)] shows that the $\mathrm{AlC_2O}$ coordination in 4 is distorted further away from an idealized planar geometry than the aluminum in 1. This is consistent with the ^{13}C NMR data. The magnitude of the change is, however, less than that expected. An examination of the crystal structure of 4 shows that, in the solid state, the 2,6-$\mathrm{Me_2py}$ ligand is oriented so as to limit the steric interaction between its methyl groups and the BHT and aluminum–methyl ligands. In addition to the increased tetrahedral nature of the aluminum core in 4, the only significant structural changes are small increases in the Al–N bond distance and Al–O–C bond angle in going from 1 to 4.

We have previously demonstrated that for a series of $\mathrm{Me_3AlPR_3}$ complexes in which the phosphines have the same cone angle, the stronger Lewis bases give stronger Al–P interactions, resulting in a downfield shift of the aluminum methyl ^{13}C resonance.[8] A similar downfield shift is observed for the ^{13}C NMR signal of aluminum–methyl in 1 and 3 (−5.10 and −5.02 ppm respectively), 4-Mepy being the stronger Lewis base of the two ligands. The relative position of 1 and 3 in Figure 1, however, suggests that electronic effects have considerably less influence than steric effects.

It is clear, therefore, that for the aryloxide complexes $\mathrm{AlMe_2(BHT)L}$ the ^{13}C NMR shift for the aluminum-methyls, and thus the geometry around Al, is dependent primarily on the steric properties and to a much lesser extent on the electronic properties of the Lewis base, L. Furthermore, the similarity in the Al–O bond distances and Al–O–C bond angles for compounds 1 and 4 suggests that the magnitude of any Al–O π-interaction is largely independent of the steric bulk of the Lewis base.

Primary and Secondary Amine Adducts of $\mathbf{AlR_2(BHT)}$ and $\mathbf{AlR(BHT)_2}$. The elimination–condensation reaction sequence (eq 3) that occurs between an aluminum-alkyl and a primary or secondary amine has been

$$\mathrm{AlR_3 + HNR'_2 \rightarrow [R_2AlNR'_2]_n + RH} \qquad (3)$$

widely explored as a route to aluminum–nitrogen ring and cluster compounds.[12] We have observed no alkyl elimination from the interaction of primary or secondary amines with aluminum compounds containing the sterically hindered aryloxide ligand BHT.

The addition of 1 equiv of either $\mathrm{HNEt_2}$ or $\mathrm{HN^iBu_2}$ to a pentane solution of $\mathrm{AlMe(BHT)_2}$ results in the isolation of the Lewis acid–base adducts, $\mathrm{AlMe(BHT)_2(HNEt_2)}$ (7) and $\mathrm{AlMe(BHT)_2(HN^iBu_2)}$ (8). No further reaction is observed, for either 7 or 8, even on prolonged heating at elevated temperatures (>110 °C). Similarly, no alkane evolution is observed from the formation of the adducts through the reaction of the primary amines $\mathrm{H_2N^tBu}$ and $\mathrm{H_2N^nBu}$ (9–16) or ammonia (17) and the aluminum aryloxide compounds $\mathrm{AlR(BHT)_2}$ and $\mathrm{AlR_2(BHT)(OEt_2)}$ (R = Me, Et).

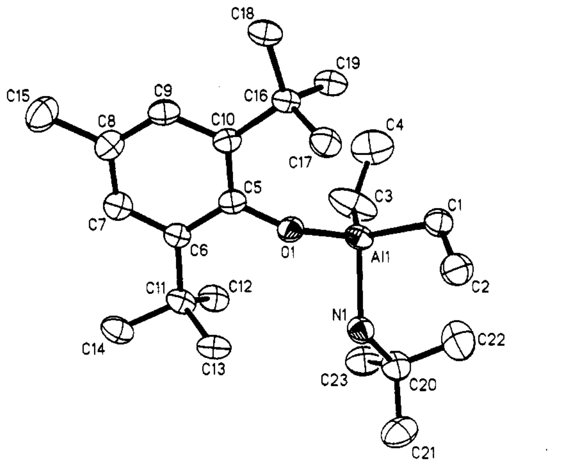
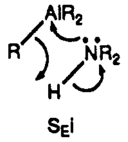


Figure 3. Structure of $\mathrm{AlEt_2(BHT)(H_2N^tBu)}$ (16). Thermal ellipsoids are drawn at the 40% level, and hydrogen atoms are omitted for clarity.



III

It has been commonly assumed that the reaction of aluminum–alkyls and Bronsted acids proceeds via the prior formation of a Lewis acid–base adduct from which the elimination reaction occurs.[13] The differences in reactivity of various Bronsted acids are rationalized in terms of the acidity of the proton in the adduct molecule. Seminal work by Beachley et al.[14] has demonstrated, however, that although aluminum–alkyls and amines do form adducts, the important step for elimination is the prior dissociation of the adduct (eq 4). If the recombination of the monomeric

$$\mathrm{R_3Al{\cdot}N(H)R'_2 \rightarrow AlR_3 + N(H)R'_2} \qquad (4)$$

aluminum compound and the amine occurs with the appropriate orientation, elimination may occur, possibly via a four-centered $\mathrm{S_Ei}$ (substitution, electrophilic, internal) mechanism (III).[15] The formation of a stable aluminum–amine adduct is therefore a "dead-end" path for alkane elimination. Thus, if the Lewis acid base adducts 6–17 are undissociated in hydrocarbon solution, no alkane elimination could occur. We have demonstrated,[16] however, that at room temperature Lewis base complexes of $\mathrm{AlMe(BHT)_2}$ exist in equilibrium with the dissociated species (eq 5). It would seem likely, therefore, that the

$$\mathrm{AlMe(BHT)_2L \rightleftharpoons AlMe(BHT)_2 + L} \qquad (5)$$

lack of any reaction between the acidic N–H and the basic Al–R ligands is either because the sterically hindered aryloxide ligand precludes the approach of the amine to the aluminum atom in the orientation required for alkane elimination[17] or because the basicity, and therefore reactivity, of the aluminum–alkyl toward a Bronsted acid is reduced by the presence of the aryloxide substituent on the aluminum.[18]

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Table II. Selected Bond Lengths (Å) and Bond Angles (deg) in $AlEt_2(BHT)(H_2N^tBu)$ (16)

Al(1)–O(1)	1.748 (3)	Al(1)–N(1)	2.039 (3)
Al(1)–C(1)	1.974 (4)	Al(1)–C(3)	1.960 (5)
O(1)–C(5)	1.362 (5)	N(1)–C(20)	1.513 (5)
C(1)–C(2)	1.536 (6)	C(3)–C(4)	1.463 (7)
O(1)–Al(1)–N(1)	97.9 (1)	O(1)–Al(1)–C(1)	112.5 (1)
O(1)–Al(1)–C(3)	114.9 (2)	N(1)–Al(1)–C(1)	99.7 (2)
N(1)–Al(1)–C(3)	109.8 (2)	C(1)–Al(1)–C(3)	118.6 (2)
Al(1)–O(1)–C(5)	151.3 (2)	Al(1)–N(1)–C(20)	128.0 (2)
Al(1)–C(1)–C(2)	117.1 (3)	Al(1)–C(3)–C(4)	122.8 (3)

Table III. Decomposition Temperatures and ^1H NMR Spectral Data for the Adducts $AlEt_2X(H_2N^tBu)$

X	dec temp, °C	^1H NMR,[a] ppm: $AlCH_2CH_3$	$AlCH_2$	$\delta_{CH_3} - \delta_{CH_2}$	χ	ref
Et	90	1.33	0.09	1.24	1.30	b
Cl	100	1.45	0.35	1.10	1.39	b
Br	120	1.62	0.57	1.05	1.42	b
I	ca. 120	1.48	0.53	0.95	1.48	b
BHT (16)	>120	1.02	0.07	0.95	1.48	c

[a] NMR spectra recorded in CCl_4 (10% $CDCl_3$). [b] Gosling, K.; Bowen, R. E. *J. Chem. Soc., Dalton Trans* **1974**, 1961. [c] This work.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) in $AlEt_2(BHT)(py{\bullet}O)$ (19)

Al(1)–O(1)	1.868 (1)	Al(1)–O(2)	1.754 (1)
Al(1)–C(1)	1.978 (2)	Al(1)–C(3)	1.970 (3)
O(1)–N(1)	1.349 (2)	O(2)–C(10)	1.354 (2)
C(1)–C(2)	1.526 (4)	C(3)–C(4)	1.509 (4)
O(1)–Al(1)–O(2)	105.5 (1)	O(1)–Al(1)–C(1)	104.0 (1)
O(1)–Al(1)–C(3)	105.0 (1)	O(2)–Al(1)–C(1)	112.1 (1)
O(2)–Al(1)–C(3)	111.2 (1)	C(1)–Al(1)–C(3)	117.8 (1)
Al(1)–O(1)–N(1)	121.8 (1)	Al(1)–O(2)–C(10)	144.1 (1)
Al(1)–C(1)–C(2)	115.2 (2)	Al(1)–C(3)–C(4)	118.5 (2)

In order to probe the relative importance of these steric and electronic effects involved in the stabilization of compounds **6**–**17** toward the thermal elimination of alkane, we have further investigated the structural and spectroscopic properties of one of these compounds, $AlEt_2(BHT)(H_2N^tBu)$ (**16**). The choice of **16** was dictated by its analogy to the adducts $AlEt_2X(H_2N^tBu)$ (X = Et, Cl, Br, I) whose stability toward alkane elimination has been described.[19]

The molecular structure of compound **16** is shown in Figure 3; selected bond lengths and angles are given in Table II. The structure consists of discrete monomeric units with no unusual bond lengths or angles. The amine ligand adopts a staggered conformation with the ^tBu group nearly anti to the BHT ligand [C(20–N(1)–Al(1)–O(1) = 164.9°].

In order for alkane elimination to occur, either directly from the complex or via a four-membered S_Ei process, one of the amine N–H bonds must be oriented coplanar with the Al–C bond of the alkyl group to be eliminated. Such a conformation would require the amine ^tBu group to eclipse either the BHT ligand or one of the ethyl groups. Although the former is undoubtably disfavored on steric grounds, it is unlikely that the latter is sufficiently sterically hindered given that the elimination of ethane occurs readily from $AlEt_3(H_2N^tBu)$,[19] in which a similar conformation must occur. This suggests that steric inhibition of alkane elimination should not be present. In fact, any steric interaction in the isolated complex will be significantly reduced in a four-centered S_Ei type transition state.

Gosling and Bowen[19] reported the correlation between NMR spectral data and thermal stabilities of adducts of the general form $AlEt_2X(H_2N^tBu)$ (X = Et, Cl, Br, I). The corresponding data for **16** are presented in Table III.

An estimate of the electronegativity of the aluminum atoms in the adducts should provide information concerning the relative degrees of polarity of the Al–C bond and therefore the relative negative charge density at the α-carbon, which should be directly related to the basicity of the aluminum ethyl group. The electronegativity may readily be estimated by using the modified Dailey–Schooleny relationship[20] (eq 6), where χ is the electronegativity of aluminum and Δ is the internal chemical shift (eq 7) of an ethyl group bonded to aluminum.

$$\chi = 0.62\Delta + 2.07 \qquad (6)$$

$$\Delta = \delta_{CH_3} - \delta_{CH_2} \qquad (7)$$

By use of this method, the calculated value of χ for **16** is the same as that found for $AlEt_2I(H_2N^tBu)$ (see Table III). This similarity is also reflected in the thermal stability of the two compounds. The high electronegativity of the aluminum atom in **16** would suggest an electron-rich aluminum center, consistent with our previous ^{27}Al NMR studies,[3] and the presence of π-donation of electron density from the BHT onto the aluminum. We propose, therefore, that this donation of electron density accounts for the reduced basicity of the aluminum–alkyl and therefore the lack of reactivity observed for adducts **6**–**17**.

Pyridine *N*-Oxide Adducts of $AlR_2(BHT)$ and $AlR(BHT)_2$. In the reaction of organoaluminum compounds with oxygen, organoaluminum alkoxides are formed via alkyl peroxide compounds (eq 8).[21] Pasynkiewicz and co-workers[22] have shown, however, that the oxidation of $AlMe(BHT)_2$ does not result in the formation of methoxy groups, but rather the BHT radical and unidentified aluminum-containing radicals are formed. In view of our recent study of the formation of the gallium and indium alkoxides, $[(^tBu)_2M(O^tBu)]_2$, from the parent trialkyl by the addition of pyridine *N*-oxide[23] (eq 9), we have investigated the analogous reactions with $AlR_2(BHT)(OEt_2)$ and $AlR(BHT)_2$ (R = Me, Et).

$$\text{Al–R} \xrightarrow{O_2} [\text{Al–OOR}] \rightarrow \text{Al–OR} \qquad (8)$$

$$M(^tBu)_3 \xrightarrow{py{\cdot}O} \tfrac{1}{2}[(^tBu)_2M(O^tBu)]_2 \qquad (9)$$

$$M = Ga, In$$

The addition of pyridine *N*-oxide (py·O) to pentane solutions of $AlR_2(BHT)(OEt_2)$ or $AlR(BHT)_2$ (R = Me, Et) yields the Lewis acid–base adducts AlR(BHT)(py·O), R = Me (**18**), Et (**19**), and $AlR(BHT)_2(py{\cdot}O)$, R = Me (**20**), Et (**21**), respectively. The complexes are stable even in refluxing toluene, showing no oxidation of the aluminum–alkyl groups. Unlike all the previous examples of Lewis acid–base complexes with aluminum–BHT compounds that we have reported,[2–4,15] compounds **18**–**21** show no ligand dissociation, whether at elevated temperatures or in the presence of an excess of a competing Lewis base, e.g., py. In addition, the py·O ligand readily displaces py from $AlMe(BHT)_2(py)$ to give **20** as the only aluminum-containing product (eq 10). This unusual affinity of alu-

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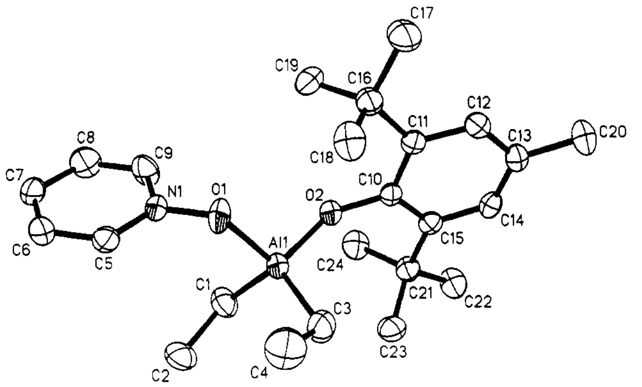


Figure 4. Structure of $AlEt_2(BHT)(py{\cdot}O)$ (**19**). Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms are omitted for clarity.

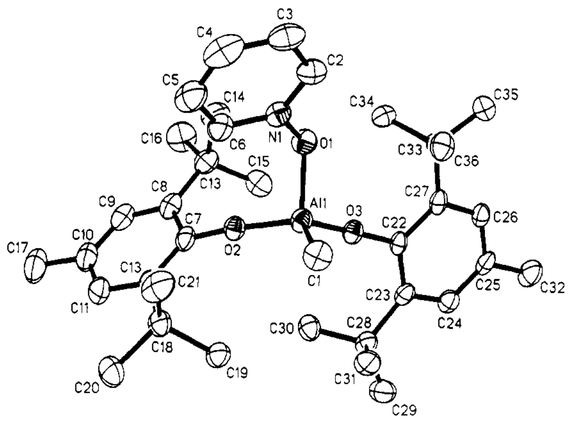


Figure 5. Structure of $AlMe(BHT)_2(py{\cdot}O){\cdot}{}^1/_2(CH_2Cl_2)$ (**20**). Thermal ellipsoids are drawn at the 40% level. Hydrogen atoms and the CH_2Cl_2 of solvation are omitted for clarity.

minum for a Lewis base prompted us to investigate the molecular structure of two of these complexes, **19** and **20**.

$$AlMe(BHT)_2(py) + py{\cdot}O \rightarrow AlMe(BHT)_2(py{\cdot}O) + py \quad (10)$$

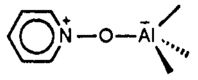
The structures of **19** and **20** have been determined by X-ray crystallography and are shown in Figures 4 and 5, respectively. Selected bond lengths and angles are given in Tables IV and V. Both structures consist of discrete monomeric units with normal intramolecular distances. The Al–C distances in **19** and **20** are within the range observed for aluminum–alkyl carbon bonds (1.90–2.01 Å).[24] Both the aryloxide Al–O distances [1.717 (3)–1.754 (1) Å] and Al–O–C bond angles [144.1 (1)–174.8 (3)°] are in the ranges observed previously and are consistent with some degree of π-bonding between oxygen and aluminum.[2,3]

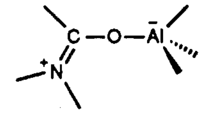
The Al–O bond distances associated with pyridine *N*-oxide ligands, in **19** and **20**, 1.868 (1) and 1.854 (4) Å, respectively, are within the range previously reported for neutral oxygen donor bases coordinated to four-coordinate aluminum (1.83–2.03 Å).[25] In particular, they compare favorably with the value observed for $Me_3AlONMe_3$ [1.857 (2) Å].[26] In addition, the acute Al–O–N angles associated with the pyridine *N*-oxide ligands [121.8 (1)° (**19**) and 122.4 (3)° (**20**)] and the torsion angle between the pyridine rings and the Al–O bond [75.9° (**19**), 48.3° (**20**)] are consistent with sp^3 hybridization at oxygen with negligible π-interaction between oxygen and either aluminum or nitrogen.

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) in $AlMe(BHT)_2(py{\bullet}O)$ (20)

Al(1)–O(1)	1.854 (4)	Al(1)–O(2)	1.739 (4)
Al(1)–O(3)	1.717 (3)	Al(1)–C(1)	1.956 (5)
O(1)–N(1)	1.359 (5)	O(2)–C(7)	1.362 (7)
O(3)–C(22)	1.360 (5)		
O(1)–Al(1)–O(2)	102.3 (2)	O(1)–Al(1)–O(3)	105.3 (2)
O(1)–Al(1)–C(1)	102.3 (2)	O(2)–Al(1)–O(3)	111.8 (2)
O(2)–Al(1)–C(1)	118.7 (2)	O(3)–Al(1)–C(1)	114.1 (2)
Al(1)–O(1)–N(1)	122.4 (3)	Al(1)–O(2)–C(7)	174.8 (3)
Al(1)–O(3)–C(22)	167.9 (3)		

One can envisage a simple resonance form for a pyridine *N*-oxide adduct of an aluminum Lewis acid in which the negative charge is centered on aluminum (IV). The


IV


V

presence of increased electron density on aluminum should be evident from an upfield shift in the ¹H NMR signal for the aluminum–methyl ligand. Such an upfield shift is indeed observed for **20** (–0.37 ppm) as compared to other Lewis acid–base adducts of $AlMe(BHT)_2$ (–0.1 to 0.2 ppm). We have also observed similar upfield shifts for amide complexes $AlMe(BHT)_2[O{=}C(NR_2)R']$,[27] for which a similar resonance form, placing negative charge at aluminum, can be drawn (V).

Resonance structure IV would also imply sp^3 hybridization at the pyridine *N*-oxide oxygen. This is indeed observed in the molecular structures of **19** and **20** (see above).

From the above crystallographic data, we propose that the Lewis base characteristics of pyridine *N*-oxide are that of a strongly σ-donating ligand. This is consistent with the lack of ligand dissociation, in solution, of the pyridine *N*-oxide in compounds **18**–**21**.

Pentafluorophenoxide Compounds of Aluminum. Interaction of $AlMe_3$ with 1 equiv of HOC_6F_5 in pentane (eq 11) yields the bridging phenoxide compound,

$$AlMe_3 + HOC_6F_5 \rightarrow {}^1/_2[Me_2Al(\mu\text{-}OC_6F_5)]_2 + MeH \quad (11)$$

$[Me_2Al(\mu\text{-}OC_6F_5)]_2$ (**22**), in a similar manner to that observed by Oliver et al. for the analogous pentafluorobenzenethiolate compound.[28] The dimeric structure of **22** is confirmed by solution molecular weight measurements.

The ¹H NMR signal for the aluminum–methyl protons of **22** (δ –0.28) exists as a sharp quintet [J(F–H) = 2.3 Hz] at room temperature (Figure 6). The coupling arises via a through-space spin–spin interaction between the aluminum–methyl protons and the four equivalent ortho fluorine atoms of the two phenoxide rings. This observation implies that the phenoxide rings are static at room temperature and are orientated perpendicular to the Al_2O_2 core.

Attempts to isolate a pyridine or substituted pyridine adduct of the pentafluorophenoxide complex were unsuccessful. However, addition of quinuclidine, $N(C_2H_4)_3CH$, to **22** results in cleavage of the phenoxide bridges to give the monomeric Lewis acid–base complex $AlMe_2$-

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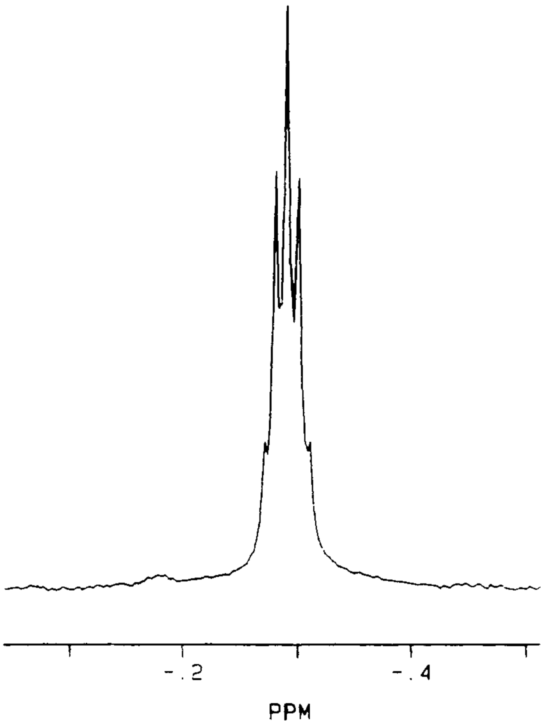

Figure 6. ^1H NMR (250 MHz) spectrum of the aluminum-methyl in $[Me_2Al(\mu\text{-}OC_6F_5)]_2$ (**22**); J(F-H) = 2.3 Hz.

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) in $AlMe_2(OC_6F_5)[N(C_2H_4)_3CH]$ (23)

Al(1)-O(1)	1.787 (1)	Al(1)-N(1)	2.002 (2)
Al(1)-C(1)	1.951 (2)	Al(1)-C(2)	1.950 (2)
O(1)-C(3)	1.327 (2)		
O(1)-Al(1)-N(1)	96.6 (1)	O(1)-Al(1)-C(1)	111.6 (1)
O(1)-Al(1)-C(2)	110.9 (1)	N(1)-Al(1)-C(1)	107.7 (1)
N(1)-Al(1)-C(2)	106.4 (1)	C(1)-Al(1)-C(2)	120.8 (2)
Al(1)-O(1)-C(3)	128.8 (1)		

$(OC_6F_5)[N(C_2H_4)_3CH]$ (**23**). Unlike **22**, the ^1H NMR signal for the aluminum-methyl protons of **23** (δ -0.53) is a singlet, exhibiting no measurable coupling to fluorine.

Our ab initio investigation[6] of the model compounds $AlH_2(OH)PH_3$ and $AlH_2(OMe)PH_3$ indicates that the degree of π-bonding between the oxygen lone pairs and the Al-P σ^*-orbital should be sensitive to the energies of the oxygen lone pairs. Substituent effects are therefore expected to be significant. For example, adding electron-withdrawing groups to the phenyl ring should result in a decrease π-donation from oxygen to aluminum. This reduced π-bonding would result in a longer Al-O bond length and a more acute Al-O-C bond angle. Given the electron-withdrawing nature of the C_6F_5 group, these changes are expected to be present in the structure of **23**.

A view of the molecular structure of **23**, as determined by X-ray crystallography, is shown in Figure 7. Selected bond lengths and angles are given in Table VI. Although the Al-C bonds in **23** [1.951 (2), 1.950 (2) Å] are short compared to those found for the other monomeric $AlMe_2(OR)L$ compounds we have studied (1.96–1.97 Å),[2,3] they are within the range observed previously for aluminum-methyl compounds (1.90–2.01 Å).[20] The Al-N bond distance [2.002 (2) Å] is also within the range previously reported for aluminum-nitrogen adduct bonds (1.88–2.09 Å).[10]

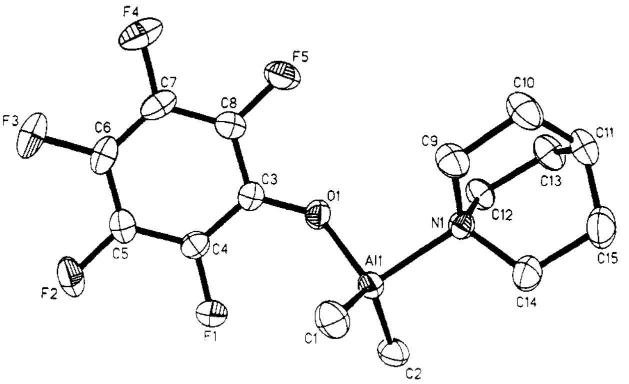

Figure 7. Structure of $AlMe_2(OC_6F_5)[N(C_2H_4)_3CH]$ (**23**). Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms are omitted for clarity.

As predicted, the presence of electron-withdrawing substituents on the aryl ring of **23** does result in the lengthening of the Al-O bond [1.787 (1) Å] and a decrease in the Al-O-C angle [128.8 (1)°], when compared to the values observed for alkyl-substituted monoaryloxide complexes, 1.70–1.74 Å and 144–164°, respectively. These changes are consistent with our prediction of little or no π-bonding between aluminum and oxygen. In fact, the orientation of the pentafluorophenyl ring derived from the ring-O-Al torsional angle [50.2°] suggests that there is also minimal interaction between the oxygen lone pairs and the π- or π^*-orbitals on the ring.

Although the molecular structure of the hexafluoroisopropoxide complex $\{Al(\mu\text{-}OH)[OCH(CF_3)_2](H_2NC_2H_4NH_2)\}_2$ has been previously reported,[29] we believe that the structure of **23** represents the first example of a fluorine-substituted aryloxide aluminum complex to be characterized crystallographically.

Relationship between Al-O Bond Distance, Al-O-C Bond Angle, and Al-O π-Bonding. For transition-metal aryloxide complexes, the short M-O bond distances and large M-O-C bond angles are frequently cited as being indicative of significant oxygen-p to metal-d π-bonding. A number of studies have shown that a definite correlation exists between the M-O bond distances and the electron configuration at the metal; i.e., the more electron-deficient the metal, the shorter the M-O bond.[30] Recent studies by Rothwell et al.[31] have shown that there is no apparent correlation between the M-O bond distance and M-O-C bond angle for aryloxides of groups 4–6. They conclude that because the M-O-C bond angle is quite flexible only the M-O distance can be used as a basis for determining the amount of oxygen-to-metal π-bonding.[26]

The Al-O bond distances and Al-O-C bond angles for a wide range of monomeric aluminum aryloxide compounds that have been structurally characterized are collected in Table VII. Figure 8 contains a plot of Al-O distances versus Al-O-C angles for monomeric four-coordinate aluminum aryloxide, $AlX_2Y(OR)$ (a) and $AlXY(BHT)_2$ (b). There is clearly a nearly linear relationship between these two variables for the monoaryloxide complexes $AlX_2Y(OR)$, suggesting that in less sterically congested complexes the Al-O bond length and the Al-O-C bond angle are related. A lack of correlation between the Al-O bond length and the Al-O-C bond angle exists, however, for compounds with more than one aryloxide bonded to aluminum. A similar result was obtained for

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Table VII. Al–O Bond Distances and Al–O–C Bond Angles for Selected Derivatives of Aluminum Aryloxides

compd	ligand	Al–O, Å	Al–O–C, deg	$\Delta_{O,C}$, Å	source
$AlMe_2(BHT)(PMe_3)$	BHT	1.736 (5)	164.5 (4)	–0.234 (5)	*a*
$[AlMeCl_2(BHT)][HNMe_3]$	BHT	1.713 (4)	164.0 (3)	–0.282 (5)	*a*
$AlMe_2(BHT)(py)$	BHT	1.740 (4)	156.1 (3)	–0.220 (6)	*b*
$AlMe_2(BHT)(2,6\text{-}Me_2py)$	BHT	1.744 (2)	158.0 (3)	–0.224 (3)	*c*
$AlMe_2(BHT)(O{=}CPh_2)$	BHT	1.731 (8)	157.7 (8)	–0.22 (1)	*d*
	$O{=}CPh_2$	1.907 (8)	153.8 (9)	–0.04 (1)	
$AlMe_2(OC_6F_5)[N(C_2H_4)_3CH]$	OC_6F_5	1.787 (1)	128.8 (1)	–0.163 (2)	*c*
$AlEt_2(BHT)(H_2N^tBu)$	BHT	1.748 (3)	151.3 (2)	–0.222 (5)	*c*
$AlEt_2(BHT)(py{\cdot}O)$	BHT	1.754 (1)	144.1 (1)	–0.220 (2)	*c*
	O·py	1.868 (1)	128.8 (1)[g]	–0.106 (2)	
$AlEt_2(BHT)[O{=}C(OMe)C_6H_4\text{-p-}Me]$	BHT	1.749 (5)	145.6 (5)	–0.215 (9)	*e*
	$O{=}C(OMe)C_6H_4\text{-}p\text{-}Me$	1.887 (6)	143.0 (6)	–0.077 (9)	
$AlMe(BHT)_2$	BHT	1.687 (2)	140.5 (2)	–0.240 (3)	*e*
		1.685 (2)	146.8 (2)	–0.242 (3)	
$AlMe(OMes)_2(3,5\text{-}Me_2py)$	OMes	1.722 (7)	140.6 (6)	–0.22 (1)	*b*
	OMes	1.714 (6)	145.8 (6)	–0.23 (1)	
$AlMe(BHT)_2[O{=}C(OMe)Ph]$	BHT	1.714 (9)	153.3 (8)	–0.25 (2)	*d*
	BHT	1.721 (8)	156.3 (6)	–0.24 (2)	
	$O{=}C(OMe)Ph$	1.851 (7)	174 (1)	–0.11 (2)	
$AlMe(BHT)_2[O{=}C(H)^tBu]$	BHT	1.726 (3)	131.3 (2)	–0.229 (4)	*d*
	BHT	1.729 (3)	140.5 (2)	–0.226 (4)	
	$O{=}C(H)^tBu$	1.920 (3)	136.0 (3)	–0.035 (4)	
$AlMe(BHT)_2[O{=}CPh_2]$	BHT	1.733 (5)	142.6 (3)	–0.209 (8)	*f*
	BHT	1.721 (6)	161.4 (5)	–0.221 (8)	
	$O{=}CPh_2$	1.903 (6)	144.0 (6)	–0.039 (8)	
$AlMe(BHT)_2(py{\cdot}O)$	BHT	1.739 (4)	174.8 (3)	–0.217 (5)	*c*
	BHT	1.717 (3)	167.9 (3)	–0.239 (5)	
	O·py	1.854 (4)	122.4 (3)[g]	–0.102 (5)	
$AlMe(BHT)_2[OC(Me)Ph_2]LiOEt_2$	BHT terminal	1.736 (2)	165.6 (2)	–0.233 (4)	*f*
	BHT bridging		146.3 (2)	–0.164 (4)	
	$OC(Me)Ph_2$ bridging	1.808 (2)	134.0 (2)	–0.161 (4)	

[a] Reference 2. [b] Reference 3. [c] This work. [d] Power, M. B.; Bott, S. G.; Clark, D. L.; Atwood, J. L.; Barron, A. R. *Organometallics* **1990**, *9*, 3086. [e] Reference 7. [f] Reference 27. [g] Al–O–N bond angle.

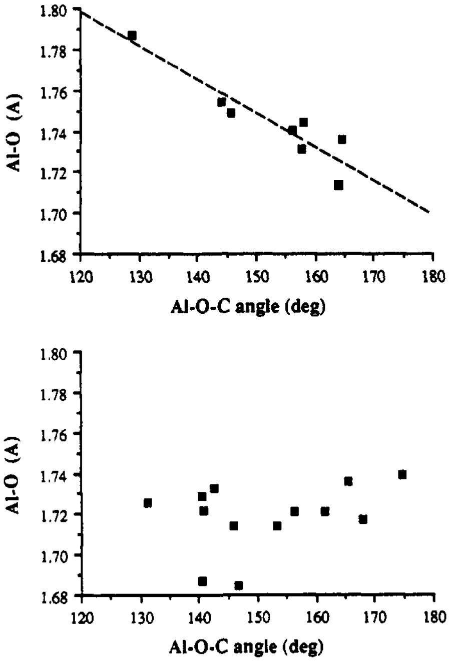
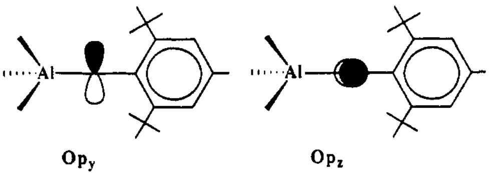


Figure 8. Plot of Al–O bond length (Å) versus Al–O–C bond angle (deg) for the terminal aryloxide ligands within the compounds $AlX_2Y(BHT)$ (a) and $AlXY(BHT)_2$ (b) listed in Table VII.

the bis(aryloxides) of the d block metals.[25] We propose that when more than one aryloxide is present at the aluminum center, steric crowding constrains the Al–O–C bond angle but does not affect the magnitude of π-bonding. A possible explanation for the relative independence of the Al–O bond distance, and presumably π-donation, from the Al–O–C bond angle is that the bond angle is controlled by the lone pair perpendicular to the phenoxide ring, p_z, rather than the lone pair parallel to the phenoxide ring, p_y (VI). It is unlikely, however, that the Al–O distance would vary significantly between either of these interactions.



VI

Rothwell et al.[25b] noted that a consideration of the covalent radii and bond lengths reported for organic molecules would predict a metal alkoxide or aryloxide σ-bond length to be 0.10–0.15 Å shorter than a metal–alkyl bond. Therefore, the parameter $\Delta_{O,C}$ was proposed (eq 12) as a

$$\Delta_{O,C} = d(M\text{–}O) - d(M\text{–}C) \tag{12}$$

probe for possible π-bonding between aryloxide, oxygen atoms, and electron-deficient metal centers. In the case of group 14 metals, $\Delta_{O,C}$ was found to be between –0.15 (Sn) and –0.17 (Ge), consistent with no π-bonding between oxygen and the metal center.[25b] On the other hand, $\Delta_{O,C}$ values for Ti and Zr were –0.28 and –0.29, indicative of significant π-bonding.[25b]

The $\Delta_{O,C}$ values for aluminum aryloxide compounds are given in Table VII; also included for comparison are the values for a bridging aryloxide and other oxygen donor ligands within the same compounds. From the data, it is clear that pyridine *N*-oxide [$\Delta_{O,C}$ = –0.102 (5), –0.106 (2) Å], is, as predicted above, within the region expected for no π-interaction. The bridging aryloxide[27] ($\Delta_{O,C}$ = –0.16 Å) and pentafluorophenoxide ($\Delta_{O,C}$ = –0.164) ligands are also consistent with negligible π-bonding. By contrast, the terminal aryloxides BHT and OMes (Mes = 2,4,6-$Me_3C_6H_2$) have much shorter Al–O bond distances [$\Delta_{O,C}$

= −0.22 (1) to −0.282 (15) Å, average −0.23 Å] than predicted based on purely σ-bonding. The values of $\Delta_{O,C}$ for these latter ligands are similar to that observed for aryloxide compounds of d^0 titanium and zirconium,[25b] in which significant pπ–dπ bonding is proposed.

An interesting point to consider is the low $\Delta_{O,C}$ values for the organic carbonyl ligands [−0.039 (8) to −0.11 (2) Å], consistent with weak Al–O bonds. This observation would be expected if, as we have predicted,[2,3,5] the short Al–O bond distances in monomeric four-coordinate aluminum aryloxide compounds are due to donation from the aryloxide oxygen p orbitals into the aluminum–carbonyl σ antiboding orbital.

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. NMR spectra in C_6D_6 were recorded on Bruker AM-250, 400, and 500 spectrometers (δ in parts per million relative to $SiMe_4$). All manipulations were carried out under nitrogen. Solvents were dried, distilled, and degassed prior to use. $AlMe_2(BHT)(OEt_2)$,[4] $AlMe(BHT)_2$,[32] $AlEt_2(BHT)(OEt_2)$,[4] $AlEt(BHT)_2$,[7] and $AlMe_2(BHT)(py)$ (1)[3] were prepared as previously described.

$AlMe_2(BHT)$(2-Mepy) (2). Method 1. To a pentane (40 mL) solution of BHT–H (2.00 g, 9.09 mmol) was added $AlMe_3$ (4.55 mL, 2.0 M solution in hexane, 9.10 mmol) via syringe. After $^1/_2$ h, 2-Mepy (1.3 mL, 13.2 mmol) was added via syringe, and the resulting solution was stirred for 2 h. Removal of the solvent in vacuo resulted in a white powder. Recrystallization from toluene (15 °C) gave colorless crystals: yield ca. 70%.

Method 2. To a pentane (20 mL) solution of $AlMe_2(BHT)(OEt_2)$ (2.00 g, 5.71 mmol), at room temperature, was added 2-Mepy (0.80 mL, 8.16 mmol) via syringe. The resulting solution was stirred for 12 h after which removal of all the volatiles under vacuum resulted in a white powder that was recrystallized from pentane/benzene: yield ca. 80%, mp = 185–186 °C. IR 1617 (m), 1571 (w), 1422 (s), 1303 (m), 1274 (s), 1221 (w), 1197 (m), 1160 (m), 1123 (w), 1114 (w), 1070 (m), 1028 (m), 971 (w), 965 (w), 952 (w), 919 (w), 868 (s), 804 (w), 779 (m), 765 (m), 727 (s), 705 (s), 672 (s), 654 (sh). ^1H NMR 8.46 [1 H, d, *J*(H–H) = 5.3 Hz, *o*-*H*, pic), 7.29 (2 H, s, C_6H_2, BHT), 6.65 [1 H, t, *J*(H–H) = 7.7 Hz, *p*-*H*, pic], 6.21 [2 H, d, *J*(H–H) = 7.7 Hz, *m*-*H*, pic], 2.50 (3 H, s, *o*-CH_3, pic), 2.36 (3 H, s, CH_3, BHT), 1.52 [18 H, s, $C(CH_3)_3$, BHT], −0.03 (6 H, s, $AlCH_3$). ^{13}C NMR 158.82 (2-*C*, pic), 155.59 (O*C*, BHT), 147.89 (6-*C*, pic), 140.20 (4-*C*, pic), 138.91 (*o*-*C*, BHT), 126.75 (*m*-*C*, BHT), 126.29 (3-C, pic), 125.43 (*p*-*C*, BHT), 121.83 (5-*C*, pic), 35.00 [$C(CH_3)_3$, BHT], 31.34 [$C(CH_3)_3$, BHT], 23.11 (CH_3, pic), 21.47 (CH_3, BHT), −3.70 ($AlCH_3$). Anal. Calcd for $C_{23}H_{36}AlNO$: C, 74.76; H, 9.82; N, 3.79. Found: C, 74.48; H, 9.95; N, 3.46.

$AlMe_2(BHT)$(4-Mepy) (3). The synthesis was carried out in an analogous manner to that of **2**: yield ca. 90%, mp = 167–169 °C. IR 1623 (m), 1420 (s), 1265 (s), 1210 (m), 1190 (m), 1123 (w), 1069 (m), 1035 (m), 923 (w), 888 (w), 861 (s), 814 (m), 776 (w), 722 (m), 695 (sh), 670 (s), 656 (s), 605 (w). ^1H NMR 8.12 [2 H, d, *J*(H–H) = 6.3 Hz, *o*-*H*, pic], 7.29 (2 H, s, C_6H_2, BHT), 6.15 [2 H, d, *J*(H–H) = 5.8 Hz, *m*-*H*, pic], 2.37 (3 H, s, CH_3, BHT), 1.56 [18 H, s, $C(CH_3)_3$, BHT], 1.48 (3 H, s, CH_3, pic), −0.04 (6 H, s, $AlCH_3$). ^{13}C NMR 155.82 (O*C*, BHT), 153.25 (*o*-*C*, pic), 146.98 (*p*-*C*, pic), 138.82 (*o*-*C*, BHT), 126.20 (*m*-*C*, pic), 125.81 (*m*-*C*, BHT), 125.36 (*m*-*C*, BHT), 35.09 [$C(CH_3)_3$, BHT], 31.28 [$C(CH_3)_3$, BHT], 21.52 (CH_3, BHT), 20.73 (CH_3, pic), −5.09 ($AlCH_3$). Anal. Calcd for $C_{23}H_{36}AlNO$: C, 74.76; H, 9.82; N, 3.79. Found: C, 74.80; H, 10.32; N, 3.71.

$AlMe_2(BHT)(2,6\text{-}Me_2py)$ (4). The synthesis was carried out in an analogous manner to that of **2** (method 1). X-ray quality crystals were obtained from toluene/pentane: yield ca. 60%, mp 159–160 °C. IR 1615 (m), 1581 (w), 1420 (s), 1273 (s), 1254 (sh), 1222 (m), 1199 (s), 1172 (m), 1124 (m), 1031 (sh), 1021 (m), 996 (sh), 973 (w), 953 (w), 919 (w), 886 (sh), 862 (s), 809 (w), 786 (m), 778 (m), 732 (sh), 720 (m), 691 (s), 671 (s), 610 (m), 574 (m), 566 (m), 543 (m). ^1H NMR 7.27 (2 H, s, C_6H_2, BHT), 6.65 [1 H, t, *J*(H–H) = 7.8 Hz, *p*-*H*, Lut], 6.19 [2 H, d, *J*(H–H) = 7.8 Hz, *m*-*H*, Lut], 2.62 (6 H, s, *o*-CH_3, Lut), 2.35 (3 H, s, CH_3, BHT), 1.51 [18 H, s, $C(CH_3)_3$, BHT], −0.02 (6 H, s, $AlCH_3$). ^{13}C NMR 159.31 (*o*-*C*, Lut), 155.85 (O*C*, BHT), 139.44 (*p*-*C*, Lut), 138.94 (*o*-*C*, BHT), 126.42 (*m*-*C*, BHT), 125.24 (*p*-*C*, BHT), 124.06 (*m*-*C*, Lut), 35.00 [$C(CH_3)_3$, BHT], 31.75 [$C(CH_3)_3$, BHT], 24.89 (CH_3, Lut), 21.48 (CH_3, BHT), −0.50 ($AlCH_3$). Anal. Calcd for $C_{24}H_{38}AlNO$: C, 75.16; H, 10.00; N, 3.65. Found: C, 75.62; H, 10.56; N, 3.57.

$AlMe_2(BHT)(NCCH_3)$ (5). To a pentane (40 mL) solution of BHT–H (2.00 g, 9.09 mmol) was added $AlMe_3$ (4.6 mL, 2.0 M solution in hexane, 9.2 mmol) via syringe. The resulting solution was stirred for $^1/_2$ h, and then CH_3CN (10 mL, excess) was added slowly via syringe. A precipitate formed after approximately 2 mL was added but redissolved by the completion of the addition. Removal of solvent in vacuo and subsequent crystallization from hexane (40 mL)/CH_3CN (10 mL) [two-phase system] resulted in pure product: yield ca. 45%, mp = 170–173 °C. IR 2322 (s), 2295 (s), 1425 (s), 1386 (s), 1362 (m), 1294 (s), 1286 (s), 1280 (s), 1233 (sh), 1217 (w), 1194 (s), 1158 (w), 1123 (w), 1097 (w), 1025 (w), 950 (w), 875 (s), 806 (m), 782 (m), 769 (w), 754 (w), 708 (sh), 681 (s), 614 (m). ^1H NMR 7.32 (2 H, s, C_6H_2, BHT), 2.44 (3 H, s, CH_3, BHT), 1.70 [18 H, s, $C(CH_3)_3$, BHT], 0.43 (3 H, s, $NCCH_3$), −0.06 (6 H, s, $AlCH_3$). ^{13}C NMR 155.28 (O*C*, BHT), 138.51 (*o*-*C*, BHT), 126.07 (*m*-*C*, BHT), 125.32 (*p*-*C*, BHT), 118.29 ($NCCH_3$), 35.02 [$C(CH_3)_3$, BHT], 31.78 [$C(CH_3)_3$, BHT], 21.50 (CH_3, BHT), −0.70 ($NCCH_3$), −5.82 ($AlCH_3$). Anal. Calcd for $C_{19}H_{32}AlNO$: C, 71.89; H, 10.16; N, 4.41. Found: C, 72.08; H, 9.81; N, 4.49.

$AlMe_2(BHT)[N(C_2H_4)_3CH]$ (6). To a pentane (40 mL) solution of $AlMe_2(BHT)(Et_2O)$ (2.00 g, 5.71 mmol) was added $N(C_2H_4)_3CH$ (0.64 g, 5.76 mmol) and the resulting solution stirred rapidly for 12 h. Removal of solvent in vacuo left a white powder that was crystallized (−20 °C) from pentane/toluene: yield ca. 90%, mp = 144–147 °C. IR 1424 (s), 1357 (m), 1293 (sh), 1282 (s), 1266 (sh), 1198 (m), 1045 (w), 1022 (w), 1004 (m), 972 (m), 898 (sh), 884 (s), 861 (m), 780 (m), 716 (m), 683 (s), 672 (s), 633 (sh), 617 (m). ^1H NMR 7.24 (2 H, s, C_6H_2, BHT), 2.63 [6 H, t *J*(H–H) = 7.9 Hz, NCH_2, quin], 2.32 (3 H, s, CH_3, BHT), 1.64 [18 H, s, $C(CH_3)_3$, BHT], 1.06 (1 H, m, *CH*, quin), 0.80 (6 H, m, NCH_2CH_2, quin), 0.23 (6 H, s, $AlCH_3$). ^{13}C NMR 156.25 (O*C*, BHT), 138.47 (*o*-*C*, BHT), 126.16 (*m*-*C*, BHT), 125.07 (*p*-*C*, BHT), 48.01 (NCH_2, quin), 35.49 [$C(CH_3)_3$, BHT], 31.59 [$C(CH_3)_3$, BHT], 24.10 (NCH_2CH_2, quin), 21.29 (CH_3, BHT), 19.23 (*C*H, quin), −4.29 ($AlCH_3$). Anal. Calcd for $C_{24}H_{42}AlNO$: C, 74.37; H, 10.92; N, 3.61. Found: C, 74.31; H, 10.19; N, 3.26.

$AlMe(BHT)_2(HNEt_2)$ (7). To a pentane (30 mL) solution of $AlMe(BHT)_2$ (2.00 g, 4.17 mmol) was added $HNEt_2$ (0.43 mL, 4.16 mmol) via syringe. Removal of volatiles in vacuo and recrystallization from pentane resulted in white needles: yield ca. 29%, mp = 112–115 °C. IR 3292 (m), 1603 (m), 1297 (sh), 1255 (s), 1202 (s), 1158 (m), 1130 (m), 1048 (m), 1037 (m), 1005 (s), 956 (w), 886 (s), 862 (s), 815 (w), 772 (s), 736 (w), 698 (s), 679 (s), 649 (s), 612 (w), 580 (w). ^1H NMR 7.18 (4 H, s, C_6H_2, BHT), 3.03 (2 H, m, CH_2, amine), 2.70 (1 H, br s, N*H*, amine), 2.29 (6 H, s, CH_3, BHT), 2.20 (2 H, m, CH_2, amine), 1.51 [36 H, s, $C(CH_3)_3$, BHT], 0.59 [6 H, t, *J*(H–H) = 7.1 Hz, CH_3, amine], 0.00 (3 H, s, $AlCH_3$). ^{13}C NMR 155.36 (O*C*, BHT), 138.27 (*o*-*C*, BHT), 126.46 (*m*-*C*, BHT), 125.82 (*p*-*C*, BHT), 43.51 (NCH_2CH_3, amine), 35.32 [$C(CH_3)_3$, BHT], 32.08 [$C(CH_3)_3$, BHT], 21.22 (CH_3, BHT), 13.90 (NCH_2CH_3, amine), −2.66 ($AlCH_3$). Anal. Calcd for $C_{35}H_{60}AlNO_2$: C, 75.90; H, 10.92; N, 2.53. Found: C, 75.64; H, 11.05; N, 2.46.

$AlMe(BHT)_2(HN^iBu_2)$ (8). **8** was synthesized in an analogous manner to **7**: yield ca. 64%, mp = 86–90 °C. IR 3290 (m), 1601 (m), 1296 (sh), 1250 (s), 1212 (sh), 1161 (w), 1122 (m), 1068 (m), 1040 (m), 981 (w), 935 (m), 922 (sh), 870 (s), 812 (m), 775 (m), 722 (w), 695 (sh), 675 (s), 640 (s), 615 (w). ^1H NMR 7.09 (4 H, s, C_6H_2, BHT), 2.28 (6 H, s, CH_3, BHT), 1.64 (4 H, m, CH_2 and *CH*, amine), 1.50 [36 H, s, $C(CH_3)_3$, BHT], 1.25 (2 H, m, CH_2, amine), 0.88 [1 H, t, *J*(H–H) = 7.1 Hz, NH, amine], 0.59 [12 H, d, *J*(H–H) = 6.4 Hz, CH_3, amine], 0.05 (3 H, s, $AlCH_3$). ^{13}C NMR 156.03 (O*C*, BHT), 138.21 (*o*-*C*, BHT), 126.20 (*m*-*C*, BHT), 125.53 (*p*-*C*, BHT), 57.25 (α-*C*, amine), 35.42 [$C(CH_3)_3$, BHT], 32.28 [$C(CH_3)_3$, BHT], 26.05 (β-*C*, amine), 21.20 (CH_3, BHT), 20.33 (β-*C*, amine), −2.48 ($AlCH_3$). Anal. Calcd for $C_{39}H_{68}AlNO_2$: C, 76.79; H, 11.24; N, 2.30. Found: C, 77.15; H, 13.06; N, 2.18.

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[32] Starowieyski, K. B.; Pasynkiewicz, S.; Skowronska-Ptasinska, M. *J. Organomet. Chem.* **1975**, *90*, C43.

Compounds 9–16 were synthesized by the addition of a slight excess of the amine to a pentane solution of the appropriate aluminum compound: $AlMe(BHT)_2$, $AlEt(BHT)_2$, $AlMe_2(BHT)(OEt_2)$, or $AlEt_2(BHT)(OEt_2)$.

$AlMe(BHT)_2(H_2N^nBu)$ (9): yield ca. 60%, mp = 116–118 °C. IR 1577 (w), 1422 (s), 1293 (sh), 1263 (s), 1235 (m), 1205 (w), 1172 (w), 1133 (vw), 1097 (w), 953 (vw), 887 (m), 860 (m), 844 (w), 775 (w), 722 (m), 691 (m), 659 (m), 623 (w). ^{1}H NMR 7.18 (4 H, s, C_6H_2, BHT), 2.93 (2 H, br m, NH_2, amine), 2.43 (2 H, br m, NCH_2, amine), 2.29 (6 H, s, CH_3, BHT), 1.55 [36 H, s, $C(CH_3)_3$, BHT], 0.80 (4 H, br m, $NCH_2CH_2CH_2$, amine), 0.59 [3 H, t, J(H–H) = 6.4 Hz, CH_3, amine], –0.14 (3 H, s, $AlCH_3$). ^{13}C NMR 154.79 (*O*C, BHT), 138.48 (*o*-C, BHT), 126.54 (*m*-C, BHT), 126.06 (*p*-C, BHT), 41.09 (NCH_2, amine), 35.19 [$C(CH_3)_3$, BHT], 33.51 (NCH_2CH_2, amine), 31.89 [$C(CH_3)_3$, BHT], 21.31 (CH_3, BHT), 19.37 ($NCH_2CH_2CH_2$, amine), 13.39 (CH_3, amine), –5.69 ($AlCH_3$). Anal. Calcd for $C_{35}H_{60}AlNO_2$: C, 75.90; H, 10.92; N, 2.53. Found: C, 75.88; H, 11.52; N, 2.44.

$AlMe(BHT)_2(H_2N^tBu)$ (10): yield ca. 70%, mp = 149–153 °C. IR 3338 (w), 3305 (w), 3285 (w), 1570 (w), 1422 (s), 1250 (s), 1203 (m), 1150 (m), 1141 (sh), 1122 (w), 1022 (m), 955 (vw), 925 (vw), 881 (s), 861 (s), 848 (m), 810 (w), 776 (m), 722 (m), 698 (s), 681 (sh), 663 (sh). ^{1}H NMR 7.18 (4 H, s, C_6H_2, BHT), 3.47 (2 H, s, NH_2, amine), 2.30 (6 H, s, CH_3, BHT), 1.54 [36 H, s, $C(CH_3)_3$, BHT], 0.90 [9 H, s, $C(CH_3)_3$, amine], –0.01 (3 H, s, $AlCH_3$). ^{13}C NMR 155.08 (*O*C, BHT), 138.41 (*o*-C, BHT), 126.58 (*m*-C, BHT), 125.98 (*p*-C, BHT), 53.15 ($C(CH_3)_3$, amine), 35.21 [$C(CH_3)_3$, BHT], 32.20 [$C(CH_3)_3$, BHT], 30.29 [$C(CH_3)_3$, amine], 21.22 (CH_3, BHT), –2.67 ($AlCH_3$). Anal. Calcd for $C_{35}H_{60}AlNO_2$: C, 75.90; H, 10.92; N, 2.53. Found: C, 74.47; H, 10.59; N, 2.38.

$AlEt(BHT)_2(H_2N^nBu)$ (11): yield ca. 50%, mp = 89–92 °C. IR 3340 (m), 3290 (w), 1751 (w), 1579 (m), 1422 (s), 1257 (s), 1240 (sh), 1202 (m), 1178 (m), 1125 (w), 1091 (m), 1070 (w), 1023 (w), 965 (sh), 950 (w), 923 (w), 884 (s), 861 (m), 810 (w), 778 (m), 822 (w), 657 (s), 638 (s), 618 (sh). ^{1}H NMR 7.19 (4 H, s, C_6H_2, BHT), 3.04 (2 H, br m, NH, amine), 2.57 (2 H, br m, NCH_2, amine), 2.30 (6 H, s, CH_3, BHT), 1.54 [36 H, s, $C(CH_3)_3$, BHT], 1.22 [3 H, t, J(H–H) = 8.1 Hz, $AlCH_2CH_3$], 0.88 (4 H, m, $NCH_2CH_2CH_2$, amine), 0.61 (6 H, m, CH_3, amine and $AlCH_2CH_3$). ^{13}C NMR 154.86 (*O*C, BHT), 138.20 (*o*-C, BHT), 126.53 (*m*-C, BHT), 126.00 (*p*-C, BHT), 41.04 (NCH_2, amine), 35.16 [$C(CH_3)_3$, BHT], 33.55 (NCH_2CH_2, amine), 31.83 [$C(CH_3)_3$, BHT], 21.29 (CH_3, BHT), 19.36 ($NCH_2CH_2CH_2$, amine), 13.36 (CH_3, amine), 10.35 ($AlCH_2CH_3$), 4.33 ($AlCH_2$). Anal. Calcd for $C_{36}H_{62}AlNO_2$: C, 76.14; H, 11.01; N, 2.47. Found: C, 75.72; H, 11.74; N, 2.44.

$AlEt(BHT)_2(H_2N^tBu)$ (12): yield ca. 70%, mp = 153–155 °C. IR 3370 (m), 3310 (m), 1770 (m), 1575 (m), 1245 (s), 1195 (s), 1145 (s), 1120 (s), 1015 (m), 983 (m), 960 (m), 921 (m), 872 (s), 855 (s), 805 (w), 772 (m), 728 (m), 720 (sh), 655 (s), 614 (s), 602 (sh). ^{1}H NMR 7.16 (4 H, s, C_6H_2, BHT), 3.45 (2 H, s, NH_2, amine), 2.28 (6 H, s, CH_3, BHT), 1.53 [36 H, s, $C(CH_3)_3$, BHT], 1.18 [3 H, t, J(H–H) = 8.0 Hz, $AlCH_2CH_3$], 0.90 [9 H, s, $C(CH_3)_3$, amine], 0.62 [2 H, q, J(H–H) = 8.0 Hz, $AlCH_2$]. ^{13}C NMR 155.40 (*O*C, BHT), 138.27 (*o*-C, BHT), 126.69 (*m*-C, BHT), 125.90 (*p*-C, BHT), 53.08 [$C(CH_3)$, amine], 35.27 [$C(CH_3)_3$, BHT], 32.29 [$C(CH_3)_3$, BHT], 30.23 [$C(CH_3)_3$, amine], 21.25 (CH_3, BHT), 9.79 ($AlCH_2CH_3$), 6.66 ($AlCH_2$). Anal. Calcd for $C_{36}H_{62}AlNO_2$: C, 76.14; H, 11.01; N, 2.47. Found: C, 76.19; H, 12.77; N, 2.34.

$AlMe_2(BHT)(H_2N^nBu)$ (13): yield ca. 60%, mp = 106–110 °C. IR 3333 (w), 3245 (m), 1583 (m), 1429 (m), 1280 (s), 1199 (m), 1172 (m), 1093 (w), 1080 (sh), 1065 (w), 1025 (w), 947 (w), 871 (s), 782 (w), 722 (sh), 690 (s), 670 (sh). ^{1}H NMR 7.22 (2 H, s, C_6H_2, BHT), 2.36 (3 H, s, CH_3, BHT), 2.18 (2 H, br, NH, amine), 2.07 (2 H, br m, NCH_2, amine), 1.54 [18 H, s, $C(CH_3)_3$, BHT], 0.74 (4 H, m, $NCH_2CH_2CH_2$), 0.62 [3 H, t, J(H–H) = 6.75 Hz, CH_3, amine], –0.37 (6 H, s, $AlCH_3$). ^{13}C NMR 155.42 (*O*C, BHT), 138.11 (*o*-C, BHT), 126.13 (*m*-C, BHT), 125.31 (*p*-C, BHT), 40.58 (NCH_2, amine), 34.90 [$C(CH_3)_3$, BHT], 33.11 (NCH_2CH_2, amine), 31.28 [$C(CH_3)_3$, BHT], 21.47 (CH_3, BHT), 19.51 ($NCH_2CH_2CH_2$, amine), 13.47 (CH_3, amine), –6.73 ($AlCH_3$). Anal. Calcd for $C_{21}H_{40}AlNO$: C, 72.16; H, 11.54; N, 4.01. Found: C, 72.23; H, 13.34; N, 4.03.

$AlMe_2(BHT)(H_2N^tBu)$ (14): yield ca. 85%, mp = 161–165 °C. IR 3325 (m), 3240 (m), 1770 (w), 1578 (m), 1425 (s), 1404 (sh), 1362 (m), 1355 (sh), 1273 (s), 1200 (s), 1151 (s), 1132 (m), 1028 (m), 1020 (sh), 930 (w), 899 (m), 865 (s), 808 (w), 794 (m), 745 (m), 692 (s), 642 (m), 610 (w), 600 (w), 579 (w). ^{1}H NMR 7.26 (2 H, s, C_6H_2, BHT), 2.49 (2 H, s, NH, amine), 2.37 (3 H, s, CH_3, BHT), 1.58 [18 H, s, $C(CH_3)_3$, BHT], 0.72 [9 H, s, $C(CH_3)_3$, amine], –0.23 (6 H, s, $AlCH_3$). ^{13}C NMR 155.46 (*O*C, BHT), 138.23 (*o*-C, BHT), 126.24 (*m*-C, BHT), 125.49 (*p*-C, BHT), 51.60 [$C(CH_3)_3$, amine], 34.98 [$C(CH_3)_3$, BHT], 31.44 [$C(CH_3)_3$, BHT], 30.16 [$C(CH_3)_3$, amine], 21.41 (CH_3, BHT), –3.50 ($AlCH_3$). Anal. Calcd for $C_{21}H_{40}AlNO$: C, 72.16; H, 11.54; N, 4.01. Found: C, 70.96; H, 11.78; N, 3.79.

$AlEt_2(BHT)(H_2N^nBu)$ (15): yield ca. 90%, mp = 110–112 °C. IR 3648 (w), 3333 (m), 3282 (m), 1750 (w), 1579 (m), 1437 (sh), 1425 (s), 1388 (s), 1377 (s), 1358 (m), 1331 (sh), 1274 (sh), 1266 (sh), 1222 (m), 1198 (m), 1165 (s), 1127 (m), 1089 (s), 1069 (m), 1017 (m), 985 (m), 953 (m), 923 (m), 874 (s), 862 (sh), 810 (m), 778 (m), 657 (s), 641 (sh), 587 (sh), 576 (m). ^{1}H NMR 7.21 (2 H, s, C_6H_2, BHT), 2.35 (3 H, s, CH_3, BHT), 2.33 (2 H, br m, NH, amine), 2.22 (2 H, m, NCH_2, amine), 1.53 [18 H, s, $C(CH_3)_3$, BHT], 1.28 [6 H, t, J(H–H) = 8.1 Hz, $AlCH_2CH_3$], 0.80 (4 H, br, $NCH_2CH_2CH_2$, amine), 0.63 (3 H, t, J(H–H) = 6.2 Hz, CH_3, amine), 0.29 [4 H, q, J(H–H) = 8.1 Hz, $AlCH_2CH_3$]. ^{13}C NMR 155.70 (*O*C, BHT), 137.93 (*o*-C, BHT), 126.14 (*m*-C, BHT), 125.33 (*p*-C, BHT), 40.78 (NCH_2, amine), 34.92 [$C(CH_3)_3$, BHT], 33.44 (NCH_2CH_2, amine), 31.24 [$C(CH_3)_3$, BHT], 21.43 (CH_3, BHT), 19.51 ($NCH_2CH_2CH_2$, amine), 13.46 (CH_3, amine), 10.15 ($AlCH_2CH_3$), 2.11 ($AlCH_2$). Anal. Calcd for $C_{23}H_{44}AlNO$: C, 73.16; H, 11.75; N, 3.71. Found: C, 71.92; H, 11.47; N, 3.17.

$AlEt_2(BHT)(H_2N^tBu)$ (16): yield ca. 90%, mp = 111–115 °C. IR 3330 (m), 3270 (w), 1575 (m), 1435 (s), 1265 (s), 1205 (m), 1142 (m), 1125 (m), 1025 (w), 1020 (sh), 980 (w), 965 (w), 922 (w), 894 (w), 865 (s), 810 (w), 783 (w), 740 (sh), 722 (w), 665 (s), 640 (s). ^{1}H NMR 7.23 (2 H, s, C_6H_2, BHT), 2.60 (2 H, s, NH_2, amine), 2.35 (3 H, s, CH_3, BHT), 1.57 [18 H, s, $C(CH_3)_3$, BHT], 1.34 [6 H, t, J(H–H) = 8.1 Hz, $AlCH_2CH_3$], 0.78 [9 H, s, $C(CH_3)_3$], 0.36 (4 H, br m, $AlCH_2$). ^{13}C NMR 155.89 (*O*C, BHT), 138.05 (*o*-C, BHT), 126.24 (*m*-C, BHT), 125.41 (*p*-C, BHT), 51.66 [$C(CH_3)_3$, amine], 35.02 [$C(CH_3)_3$, BHT], 31.48 [$C(CH_3)_3$, BHT], 30.23 [$C(CH_3)_3$, amine], 21.38 (CH_3, BHT), 9.97 ($AlCH_2CH_3$), 4.33 ($AlCH_2$). Anal. Calcd for $C_{23}H_{44}AlNO$: C, 73.16; H, 11.75; N, 3.71. Found: C, 72.71; H, 13.18; N, 3.66.

$AlMe(BHT)_2(NH_3)$ (17). To a rapidly stirred pentane solution of $AlMe(BHT)_2$ (2.01 g, 4.19 mmol) at –78 °C was added ammonia (excess) from a lecture cylinder. After 15 min, a large amount of precipitate had formed and the addition was stopped. The reaction mixture was allowed to warm slowly to room temperature and then stirred for a further 12 h. Removal of solvent in vacuo led to a white powder that was crystallized from pentane/toluene: yield 65%, mp = 170–175 °C. IR 3644 (w), 3261 (w), 1603 (w), 1421 (s), 1296 (sh), 1260 (s), 1202 (w), 1124 (w), 1094 (w), 1077 (w), 1025 (m), 894 (s), 867 (m), 859 (sh), 804 (m), 775 (m), 720 (sh), 710 (s), 667 (m), 602 (w), 577 (w), 464 (w). ^{1}H NMR 7.20 (4 H, s, C_6H_2, BHT), 2.31 (6 H, s, CH_3, BHT), 1.69 (3 H, s, NH_3, amine), 1.50 [36 H, s, $C(CH_3)_3$, BHT], –0.31 (3 H, s, $AlCH_3$). ^{13}C NMR 154.53 (*O*C, BHT), 138.66 (*o*-C, BHT), 126.45 (*m*-C, BHT), 35.12 [$C(CH_3)_3$, BHT], 31.80 [$C(CH_3)_3$, BHT], 21.31 (CH_3, BHT), –4.52 ($AlCH_3$). Anal. Calcd for $C_{31}H_{52}AlNO_2$: C, 74.80; H, 10.53; N, 2.81. Found: C, 72.55; H, 10.31; N, 2.72.

$AlMe_2(BHT)(py{\cdot}O)$ (18). Pentane (30 mL) was added to a Schlenk flask charged with $AlMe_2(BHT)(OEt_2)$ (1.50 g, 4.29 mmol) and py·O (0.43 g, 4.52 mmol). The solution was stirred for 48 h. The resulting precipitate was collected by filtration and dried in vacuo: yield ca. 40%, mp = 196–197 °C (dec). IR 1427 (m), 1295 (m), 1260 (w), 1248 (w), 1218 (m), 1201 (sh), 1189 (w), 1178 (w), 1170 (sh), 1155 (w), 1099 (w), 1073 (w), 1050 (w), 1029 (w), 973 (vw), 931 (vw), 877 (m), 870 (m), 835 (m), 822 (sh), 806 (w), 780 (w), 773 (m), 722 (m), 693 (w), 666 (m), 657 (m). ^{1}H NMR 7.58 [2 H, d, J(H–H) = 6.1 Hz, *o*-H, py·O], 7.36 (2 H, s, C_6H_2, BHT), 6.09 [1 H, t, J(H–H) = 7.6 Hz, *p*-H, py·O], 5.81 [2 H, t, J(H–H) = 6.9 Hz, *p*-H, py·O], 2.43 (3 H, s, CH_3, BHT), 1.79 [18 H, s, $C(CH_3)_3$, BHT], –0.25 (6 H, s, $AlCH_3$). ^{13}C NMR 156.31 (*O*C, BHT), 139.97 (*o*-C, py·O), 138.96 (*o*-C, BHT), 133.22 (*m*-C, py·O), 126.14 (*m*-C, BHT), 125.96 (*p*-C, py·O), 124.77 (*p*-C, BHT), 35.33 [$C(CH_3)_3$, BHT], 31.50 [$C(CH_3)_3$, BHT], 21.58 (CH_3, BHT), –6.83 ($AlCH_3$). Anal. Calcd for $C_{22}H_{34}AlNO_2$: C, 71.12; H, 9.23; N, 3.77. Found: C, 70.24; H, 8.59; N, 3.50.

$AlEt_2(BHT)(py{\cdot}O)$ (19). 19 was synthesized in a manner analogous to 17 with $AlEt_2(BHT)(ET_2O)$ (1.50 g, 3.97 mmol) and py·O (0.41 g, 4.31 mmol). Crystals were grown from pentane/

Table VIII. Summary of X-ray Diffraction Data

compound	$AlMe_2(BHT)$-(2,6-Me_2py) (**4**)	$AlEt_2(BHT)$-(H_2N^tBu) (**16**)	$AlEt_2(BHT)$-(py·O) (**19**)	AlMe(BHT)-(py·O) (**20**)	$AlMe_2(OC_6F_5)$-[$N(C_2H_4)CH$] (**23**)
empir formula	$C_{24}H_{38}AlNO$	$C_{23}H_{44}AlNO$	$C_{24}H_{38}AlNO_2$	$C_{36}H_{54}AlNO_3\cdot{}^1/_2(CH_2Cl_2)$	$C_{15}H_{19}AlF_5NO$
cryst size, mm	0.33 × 0.43 × 0.47	0.23 × 0.33 × 0.43	0.37 × 0.43 × 0.47	0.33 × 0.33 × 0.37	0.27 × 0.43 × 0.50
cryst system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$C2/c$	$P\bar{1}$
a, Å	9.994 (2)	9.025 (2)	9.630 (2)	25.025 (4)	6.9822 (6)
b, Å	21.647 (4)	13.862 (2)	18.232 (4)	16.877 (3)	9.4896 (8)
c, Å	10.822 (2)	19.339 (4)	13.980 (3)	19.261 (5)	12.7230 (9)
α, deg					93.140 (6)
β, deg	93.74 (2)	96.60 (1)	101.62 (2)	117.59 (2)	94.650 (6)
γ, deg					102.580 (7)
vol, $Å^3$	2336.3 (8)	2403.3 (7)	2404.1 (9)	7209 (2)	817.80 (1)
Z	4	4	4	8	2
density (calcd), g/cm^3	1.09	1.04	1.104	1.139	1.427
abs coeff, mm^{-1}	0.095	0.091	0.097	0.160	0.170
radiation	Mo Kα (λ = 0.71073 Å), graphite monochromator				
temp, K	198	183	173	193	183
2θ range, deg	4.0–50.0	4.0–45.0	4.0–50.0	4.0–45.0	4.0–50.0
index ranges	$0 \le h \le 11$ $0 \le k \le 25$ $-12 \le l \le 12$	$0 \le h \le 16$ $0 \le k \le 14$ $-20 \le l \le 20$	$0 \le h \le 11$ $0 \le k \le 21$ $-16 \le l \le 16$	$0 \le h \le 26$ $-11 \le k \le 11$ $-15 \le l \le 15$	$0 \le h \le 26$ $0 \le k \le 18$ $-20 \le l \le 18$
no. collected	4379	3565	4696	5071	3170
no. ind	3732	2848	3949	4139	2792
no. obsd	3365 ($\lvert F_o\rvert > 2.0\sigma\lvert F_o\rvert$)	2249 [($\lvert F_o\rvert > 4.0\sigma(\lvert F_o\rvert)$]	3949 ($\lvert F_o\rvert > 0$)	3247 [($\lvert F_o\rvert > 3.0\sigma(\lvert F_o\rvert)$]	2792 ($\lvert F_o\rvert > 0$)
weighting scheme	$w^{-1} = \sigma^2(\lvert F_o\rvert) + 0.0012(\lvert F_o\rvert)^2$	$w^{-1} = \sigma^2(\lvert F_o\rvert) + 0.0005(\lvert F_o\rvert)^2$	$w^{-1} = \mathrm{R}^2(\lvert F_o\rvert + 0.0005(\lvert F_o\rvert)^2$	$w^{-1} = \sigma^2(\lvert F_o\rvert + 0.0010(\lvert F_o\rvert)^2$	$w^{-1} = \sigma^2(\lvert F_o\rvert + 0.0002(\lvert_{Fo}\rvert)^2$
final R indexes	R = 0.058 R_w = 0.066	R = 0.060 R_w = 0.068	R = 0.055 R_w = 0.055	R = 0.073 R_w = 0.077	R = 0.039 R_w = 0.044
largest diff peak, e $Å^{-3}$	0.26	0.29	0.29	0.31	0.27

toluene: yield ca. 50%, mp = 188–190 °C (dec). IR 1423 (s), 1280 (m), 1265 (m), 1260 (m), 1220 (m), 1201 (w), 1192 (w), 977 (w), 954 (w), 867 (m), 859 (m), 841 (m), 807 (w), 783 (w), 775 (m), 722 (m), 675 (m), 637 (s), 606 (m), 589 (m), 564 (w), 531 (w). ^{1}H NMR 7.76 [2 H, d, J(H–H) = 6.3 Hz, *o-H*, py·O], 7.32 (2 H, s, C_6H_2, BHT), 6.12 [1 H, t, J(H–H) = 7.7 Hz, *p-H*, py·O], 5.88 [2 H, t, J(H–H) = 6.9 Hz, *m-H*, py·O], 2.40 (3 H, s, CH_3, BHT), 1.73 [18 H, s, $C(CH_3)_3$, BHT], 1.41 [6 H, t, J(H–H) = 8.2 Hz, $AlCH_2CH_3$], 0.49 [4 H, q, J(H–H) = 8.1 Hz, $AlCH_2$]. ^{13}C NMR 156.55 (*O*C, BHT), 139.78 (*o-C*, py·O), 138.86 (*o-C*, BHT), 133.63 (*m-C*, py·O), 126.13 (*m-C*, BHT), 126.03 (*p-C*, py·O), 124.78 (*p-C*, BHT), 35.30 ($C(CH_3)_3$, BHT), 31.48 ($C(CH_3)_3$, BHT), 21.53 (CH_3, BHT), 10.43 ($AlCH_2CH_3$), 2.58 ($AlCH_2CH_3$). Anal. Calcd for $C_{24}H_{38}AlNO_2$: C, 72.14; H, 9.59; N, 3.50. Found: C, 71.95; H, 9.52; N, 3.47.

AlMe(BHT)$_2$(py·O) (20). AlMe(BHT)$_2$ (2.00 g, 4.17 mmol) and pyridine *N*-oxide (0.80 g, 8.41 mmol) were placed as solids into a Schlenk tube. Pentane (30 mL) was added, and the resulting solution was stirred for 12 h. The white precipitate that formed was then collected and dried in vacuo: yield ca. 50%, mp = 147–149 (dec). IR 1422 (s), 1298 (m), 1286 (s), 1246 (m), 1216 (m), 1210 (sh), 1179 (w), 1172 (m), 1156 (w), 1124 (w), 1025 (w), 1014 (w), 954 (w), 930 (w), 924 (w), 892 (s), 863 (m), 838 (m), 808 (w), 767 (s), 722 (m), 685 (sh), 673 (s), 646 (s). ^{1}H NMR 7.68 [2 H, d J(H–H) = 6.2 Hz, *o-H*, py·O], 7.28 (4 H, s, C_6H_2, BHT), 6.16 (1 H, m, *p-H*, py·O), 5.89 [2 H, t, J(H–H) = 6.80 Hz, *m-H*, py·O], 2.34 (6 H, s, CH_3, BHT), 1.72 [36 H, S, $C(CH_3)_3$, BHT], –0.37 (3 H, s, $AlCH_3$). ^{13}C NMR 155.40 (*O*C, BHT), 140.55 (*o-C*, O·py), 139.28 (*o-C*, BHT), 135.29 (*m-C*, py·O), 126.43 (*m-C*, BHT), 126.30 (*p-C*, py·O), 125.29 (*p-C*, BHT), 35.54 ($C(CH_3)_3$, BHT), 32.12 ($C(CH_3)_3$, BHT), 21.43 (CH_3, BHT), –6.98 ($AlCH_3$). Anal. Calcd for $C_{35}H_{54}AlNO_3$: C, 74.56; H, 9.66; N, 2.48. Found: C, 73.86; H, 9.12; N, 3.71.

AlEt(BHT)$_2$(py·O) (21). The synthesis was carried out in an analogous manner to that for **19** with AlEt(BHT)$_2$ (2.03 g, 4.11 mmol) and py·O (0.82 g, 8.62 mmol): yield ca. 50%, mp = 91–95 °C. IR 1602 (w), 1420 (s), 1292 (sh), 1265 (s), 1260 (sh), 1222 (s), 1203 (m), 1177 (w), 1164 (m), 1154 (m), 1125 (w), 1070 (w), 1025 (m), 1014 (m), 990 (w), 964 (w), 954 (w), 928 (w), 882 (s), 865 (m), 842 (s), 811 (w), 770 (s), 728 (m), 694 (w), 674 (m), 645 (sh), 629 (s), 610 (s), 576 (w), 546 (w). ^{1}H NMR 7.89 [2 H, d, J(H–H) = 6.2 Hz, *o*-H, py·O], 7.31 (4 H, s, C_6H_2, BHT), 6.15 [1 H, t, J(H–H) = 7.8 Hz, *p-H*, py·O], 5.90 [2 H, t, J(H–H) = 7.4 Hz, *m-H*, py·O], 2.34 (6 H, s, CH_3, BHT), 1.72 [36 H, s, $C(CH_3)_3$, BHT], 1.27 [3 H, t, J(H–H) = 8.1 Hz, $AlCH_2CH_3$], 0.29 [2 H, q, J(H–H) = 8.0 Hz, $AlCH_2$]. ^{13}C NMR 155.40 (*O*C, BHT), 140.38 (*o-C*, py·O), 139.14 (*o-C*, BHT), 135.41 (*m-C*, py·O), 126.51 (*m-C*, BHT), 125.33 (*p-C*, py·O), 122.48 (*p-C*, BHT), 35.56 [$C(CH_3)_3$, BHT], 32.12 [$C(CH_3)_3$, BHT], 21.42 (CH_3, BHT), 10.66 ($AlCH_2CH_3$), 3.37 ($AlCH_2$). Anal. Calcd for $C_{37}H_{56}AlNO_3$: C, 75.34; H, 9.57; N, 2.37. Found: C, 74.48; H, 8.96; N, 3.73.

Table IX. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (×10^4 Å^2) of the Non-Hydrogen Atoms in AlMe$_2$(BHT)(2,6-Me$_2$py) (4)

	x	y	z	U(eq)^a
Al(1)	532.3 (0.7)	3125.9 (0.3)	4741.5 (0.7)	319 (2)
O(1)	–767 (2)	3631 (1)	4283 (1)	322 (5)
N(1)	1125 (2)	3452 (1)	6495 (2)	295 (6)
C(1)	2254 (3)	3179 (2)	3958 (3)	473 (10)
C(2)	–26 (4)	2256 (1)	4654 (4)	554 (12)
C(3)	–1957 (2)	3819 (1)	3732 (2)	265 (7)
C(4)	–1078 (2)	3936 (1)	2431 (2)	302 (7)
C(5)	–3318 (3)	4125 (1)	1914 (2)	321 (8)
C(6)	–4420 (2)	4220 (1)	2584 (2)	327 (8)
C(7)	–4265 (3)	4122 (1)	3844 (2)	313 (8)
C(8)	–3074 (2)	3924 (1)	4454 (2)	286 (7)
C(9)	–913 (3)	3856 (1)	1582 (2)	408 (9)
C(10)	269 (3)	4274 (2)	2021 (3)	495 (11)
C(11)	–501 (4)	3177 (2)	1529 (3)	576 (12)
C(12)	–1307 (4)	4054 (2)	243 (3)	600 (14)
C(13)	–5754 (3)	4409 (2)	1953 (3)	512 (11)
C(14)	–3024 (2)	3822 (1)	5867 (2)	327 (8)
C(15)	–1962 (3)	4235 (1)	6525 (3)	374 (9)
C(16)	–4364 (3)	3977 (2)	6428 (3)	458 (11)
C(17)	–2744 (4)	3140 (1)	6168 (3)	496 (11)
C(18)	1656 (2)	4030 (1)	6590 (2)	299 (7)
C(19)	2261 (3)	4248 (1)	7679 (3)	445 (10)
C(20)	2328 (4)	3882 (2)	8710 (3)	604 (12)
C(21)	1768 (3)	3310 (2)	8637 (3)	495 (11)
C(22)	1173 (2)	3095 (1)	7538 (2)	359 (8)
C(23)	577 (4)	2460 (2)	7510 (4)	605 (13)
C(24)	1601 (3)	4451 (1)	5489 (3)	418 (10)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogoalized $\mathbf{U}_{ij}$ tensor.

Table X. Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameter (×10⁴ Å²) of the Non-Hydrogen Atoms in $AlEt_2(BHT)(H_2N^tBu)$

	x	*y*	*z*	*U*(eq)[a]
Al(1)	1532 (1)	2407 (1)	1081 (1)	326 (4)
O(1)	901 (3)	2990 (2)	1794 (1)	315 (9)
N(1)	3534 (3)	1945 (2)	1563 (2)	353 (12)
C(1)	2234 (5)	3321 (3)	406 (2)	365 (14)
C(2)	3578 (5)	3957 (3)	664 (2)	441 (16)
C(3)	331 (6)	1298 (3)	726 (3)	747 (22)
C(4)	−873 (6)	1373 (4)	153 (3)	725 (22)
C(5)	−180 (4)	3180 (3)	2211 (2)	276 (13)
C(6)	−122 (4)	2738 (3)	2875 (2)	266 (13)
C(7)	−1256 (4)	2919 (3)	3281 (2)	325 (14)
C(8)	−2432 (4)	3534 (3)	3074 (2)	346 (15)
C(9)	−2428 (4)	3991 (3)	2441 (2)	323 (14)
C(10)	−1316 (4)	3854 (3)	2004 (2)	279 (13)
C(11)	1198 (4)	2082 (3)	3160 (2)	321 (14)
C(12)	1147 (5)	1143 (3)	2738 (2)	385 (15)
C(13)	2678 (4)	2634 (3)	3157 (2)	373 (14)
C(14)	1131 (5)	1787 (3)	3920 (2)	436 (16)
C(15)	−3623 (5)	3724 (3)	3541 (2)	523 (18)
C(16)	−1365 (4)	4460 (3)	1336 (2)	298 (13)
C(17)	113 (4)	5014 (3)	1327 (2)	355 (14)
C(18)	−2595 (5)	5222 (3)	1284 (2)	386 (15)
C(19)	−1677 (5)	3820 (3)	689 (2)	379 (15)
C(20)	4563 (5)	1192 (3)	1314 (2)	421 (16)
C(21)	6099 (5)	1326 (3)	1711 (3)	563 (19)
C(22)	4634 (6)	1328 (3)	543 (2)	656 (21)
C(23)	3946 (5)	206 (3)	1463 (3)	552 (19)

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

Table XI. Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (×10⁴ Å²) of the Non-Hydrogen Atoms in $AlEt_2(BHT)(py \bullet O)$ (19)

	x	*y*	*z*	*U*(eq)[a]
Al(1)	725.9 (0.6)	−16.4 (0.3)	2430.8 (0.4)	287 (2)
O(1)	2362 (1)	−437 (1)	3174 (1)	365 (5)
O(2)	167 (1)	636 (1)	3194 (1)	286 (4)
N(1)	2388 (2)	−1138 (1)	3487 (1)	266 (5)
C(1)	−613 (3)	−848 (1)	2142 (2)	413 (8)
C(2)	−300 (3)	−1390 (1)	1382 (2)	474 (9)
C(3)	1354 (3)	456 (1)	1324 (2)	462 (9)
C(4)	2651 (3)	158 (2)	1006 (2)	627 (11)
C(5)	3060 (2)	−1637 (1)	3048 (1)	302 (6)
C(6)	3138 (2)	−2350 (1)	3360 (2)	355 (7)
C(7)	2519 (2)	−2549 (1)	4126 (2)	367 (7)
C(8)	1837 (3)	−2023 (1)	4565 (2)	461 (8)
C(9)	1783 (2)	−1315 (1)	4238 (2)	405 (7)
C(10)	3 (2)	1363 (1)	3333 (1)	242 (6)
C(11)	1091 (2)	1768 (1)	3951 (1)	257 (6)
C(12)	889 (2)	2522 (1)	4050 (1)	290 (6)
C(13)	−323 (2)	2887 (1)	3585 (1)	290 (6)
C(14)	−1389 (2)	2474 (1)	3021 (1)	281 (6)
C(15)	−1290 (2)	1716 (1)	2896 (1)	264 (6)
C(16)	2472 (2)	1411 (1)	4501 (1)	333 (6)
C(17)	3367 (3)	1940 (2)	5230 (2)	535 (9)
C(18)	3398 (2)	1194 (1)	3773 (2)	437 (8)
C(19)	2140 (3)	748 (1)	5098 (2)	412 (8)
C(20)	−502 (3)	3701 (1)	3733 (2)	420 (8)
C(21)	−2582 (2)	1293 (1)	2326 (1)	320 (6)
C(22)	−3909 (2)	1783 (1)	2061 (2)	434 (8)
C(23)	−2301 (3)	1002 (1)	1355 (2)	410 (8)
C(24)	−2972 (2)	663 (1)	2955 (2)	410 (8)

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

Table XII. Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (×10⁴ Å²) of the Non-Hydrogen Atoms in $AlMe(BHT)_2(py \bullet O) \bullet {}^1/_2CH_2Cl_2$ (20)

	x	*y*	*z*	*U*(eq)[a]
Al(1)	2840 (1)	127 (1)	3393 (1)	364 (7)
O(1)	2509 (1)	54 (2)	2312 (2)	428 (16)
O(2)	2229 (1)	−108 (2)	3553 (2)	381 (15)
O(3)	3388 (1)	−591 (2)	3752 (2)	368 (15)
N(1)	2171 (2)	644 (2)	1827 (2)	378 (19)
C(1)	3151 (2)	1210 (3)	3593 (3)	509 (27)
C(2)	2302 (2)	847 (3)	1256 (3)	457 (26)
C(3)	1970 (3)	1431 (3)	735 (3)	556 (28)
C(4)	1517 (3)	1807 (3)	837 (4)	650 (33)
C(5)	1391 (3)	1570 (3)	1420 (4)	601 (30)
C(6)	1722 (2)	980 (3)	1924 (3)	505 (27)
C(7)	1788 (2)	−308 (3)	3746 (3)	388 (23)
C(8)	1443 (2)	−1006 (3)	3438 (3)	427 (24)
C(9)	982 (2)	−1171 (3)	3632 (3)	509 (26)
C(10)	849 (2)	−696 (4)	4113 (4)	565 (29)
C(11)	1193 (2)	−16 (3)	4416 (3)	521 (27)
C(13)	1661 (2)	193 (3)	4241 (3)	412 (23)
C(13)	1552 (2)	−1592 (3)	2904 (3)	473 (26)
C(14)	1455 (3)	−1190 (4)	2135 (3)	611 (28)
C(15)	2186 (2)	−1932 (3)	3327 (3)	549 (29)
C(16)	1117 (3)	−2301 (3)	2658 (4)	719 (35)
C(17)	334 (3)	−893 (4)	4297 (4)	814 (37)
C(18)	1996 (2)	986 (3)	4571 (3)	463 (25)
C(19)	2673 (2)	854 (3)	5067 (3)	442 (25)
C(20)	1779 (3)	1387 (4)	5118 (4)	705 (33)
C(21)	1866 (3)	1558 (3)	3893 (3)	625 (29)
C(22)	3901 (2)	−1033 (3)	4042 (3)	305 (21)
C(23)	4229 (2)	−1179 (3)	4853 (3)	357 (23)
C(24)	4739 (2)	−1663 (3)	5113 (3)	410 (24)
C(25)	4938 (2)	−1998 (3)	4625 (3)	409 (24)
C(26)	4620 (2)	−1824 (3)	3840 (3)	380 (24)
C(27)	4103 (2)	−1358 (3)	3521 (3)	357 (23)
C(28)	4072 (2)	−807 (3)	5466 (3)	396 (24)
C(29)	4498 (3)	−1066 (3)	6303 (3)	570 (28)
C(30)	3434 (2)	−1053 (3)	5313 (3)	467 (25)
C(31)	4134 (2)	100 (3)	5444 (3)	481 (26)
C(32)	5499 (2)	−2512 (3)	4939 (3)	618 (29)
C(33)	3782 (2)	−1202 (3)	2638 (3)	359 (23)
C(34)	3134 (2)	−1519 (3)	2271 (3)	419 (23)
C(35)	4089 (2)	−1623 (3)	2208 (3)	544 (27)
C(36)	3818 (2)	−311 (3)	2491 (3)	476 (26)
C(37)	0	532 (5)	2500	758 (49)
Cl(1)	176 (1)	1091 (1)	1883 (1)	1302 (13)

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

$[Me_2Al(\mu\text{-}OC_6F_5)]_2$ (22). To a pentane (40 mL) solution of HOC_6F_5 (0.50 g, 2.72 mmol) was added $AlMe_3$ (1.36 mL, 2.0 M solution in hexane, 2.72 mmol) via syringe. The resulting solution was stirred 12 h at room temperature, and then the solvent was removed in vacuo at 0 °C. Crystals were grown from pentane: yield 83%, mp = 159–165 °C. IR 1515 (s), 1307 (w), 1257 (w), 1201 (m), 1150 (m), 1016 (sh), 992 (s), 803 (sh), 717 (s), 585 (m), 545 (w), 475 (w). ^1H NMR −0.28 [12 H, quin, *J*(H–H) = 2.3 Hz, $AlCH_3$]. ^{13}C NMR 139.44 (*o*-*C*, dm, *J*($C–F_\alpha$) = 240.7 Hz), 138.30 (*m*-*C*, d, *J*($C–F_\alpha$) = 251.9 Hz, *J*($C–F_\beta$) = 14.0 Hz), 137.05 (*p*-*C*, d, *J*($C–F_\alpha$) = 251.5 Hz, *J*($C–F_\beta$) = 14.0 Hz), 127.38 (O*C*, t, *J*($C–F_\beta$) = 14.1 Hz), −10.66 ($AlCH_3$). Anal. Calcd for $C_{16}H_{12}Al_2F_{10}O_2$: C, 40.01; H, 2.52. Found: C, 39.67; H, 2.85.

$AlMe_2(OC_6F_5)[N(C_2H_4)_3CH]$ (23). To a pentane (40 mL) solution of HOC_6F_5 (1.00 g, 5.43 mmol) was added $AlMe_3$ (2.72 mL, 2.0 M solution in hexane, 5.44 mmol) via syringe. The resulting solution was stirred for $^1/_2$ h, during which time a white solid precipitated from the solution; $N(C_2H_4)_3CH$ (0.60 g, 5.40 mmol) was then added. The precipitate rapidly dissolved, and the solution was stirred for 4 h. Removal of solvent in vacuo and recrystallization from pentane (40 mL)/CH_2Cl_2 (5 mL) resulted in X-ray quality crystals: yield ca. 90%, mp = 77–79 °C. IR 1654 (w), 1520 (s), 1509 (s), 1488 (m), 1341 (m), 1316 (m), 1284 (w), 1262 (w), 1249 (w), 1190 (m), 1192 (m), 1177 (m), 1120 (w), 1025 (s), 1011 (sh), 1000 (s), 981 (s), 977 (s), 900 (w), 829 (m), 796 (m), 726 (sh), 718 (s), 686 (s), 667 (sh). ^1H NMR 2.53 (6 H, t, *J*(H–H) = 7.7 Hz, NCH_2, quin), 1.14 (1 H, m, C*H*, quin), 0.89 (6 H, m, NCH_2CH_2, quin), −0.53 (6 H, s, $AlCH_3$). ^{13}C NMR 141.02 [*o*-*C*, dm, *J*($C–F_\alpha$) = 233.8 Hz, phenol], 138.68 [*m*-*C*, dm, *J*($C–F_\alpha$) = 245.0 Hz, phenol], 136.16 [O*C*, t, *J*($C–F_\beta$) = 13.9 Hz, phenol], 133.36 [*p*-*C*, dd, *J*($C–F_\alpha$) = 238.8 Hz, *J*($C–F_\beta$) = 13.9 Hz, phenol], 45.78 (NCH_2, quin), 23.79 (NCH_2CH_2, quin), 19.69 (*C*H, quin), −12.17 ($AlCH_3$). Anal. Calcd for $C_{15}H_{19}AlF_5NO$: C, 51.28; H, 5.45; N, 3.99. Found: C, 51.19; H, 5.44; N, 3.93.

Table XIII. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (×10^4 Å^2) of the Non-Hydrogen Atoms in AlMe$_2$(OC$_6$F$_5$)[N(C$_2$H$_4$)$_3$CH] (23)

	x	y	z	U(eq)[a]
Al(1)	890 (1)	7843 (1)	8501 (1)	262 (2)
O(1)	−1010 (2)	7736 (1)	7452 (1)	311 (4)
N(1)	2138 (2)	6338 (1)	7854 (1)	255 (4)
C(1)	2804 (3)	9691 (2)	8592 (2)	396 (7)
C(2)	−205 (3)	7062 (2)	9765 (2)	383 (7)
C(3)	−1608 (2)	8804 (2)	6987 (1)	262 (5)
C(4)	−2077 (2)	9957 (2)	7550 (1)	281 (5)
C(5)	−2689 (3)	11067 (2)	7066 (1)	319 (6)
C(6)	−2860 (3)	11054 (2)	5982 (2)	353 (6)
C(7)	−2448 (3)	9920 (2)	5398 (1)	349 (6)
C(8)	−1838 (2)	8820 (2)	5891 (1)	301 (6)
C(9)	2966 (3)	6784 (2)	6839 (2)	382 (7)
C(10)	3856 (4)	5624 (2)	6326 (2)	438 (7)
C(11)	3729 (3)	4366 (2)	7034 (2)	379 (6)
C(12)	650 (3)	4931 (2)	7612 (2)	318 (6)
C(13)	1572 (3)	3740 (2)	7167 (2)	401 (7)
C(14)	3786 (3)	6072 (2)	8597 (2)	416 (7)
C(15)	4773 (4)	4944 (3)	8115 (2)	492 (8)
F(1)	−1920 (2)	9988 (1)	8613 (1)	388 (4)
F(2)	−3084 (2)	12172 (1)	7646 (1)	460 (4)
F(3)	−3432 (2)	12147 (1)	5503 (1)	522 (4)
F(4)	−2612 (2)	9897 (1)	4332 (1)	506 (4)
F(5)	−1409 (2)	7731 (1)	5295 (1)	435 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

X-ray Crystallographic Studies. A crystal data summary is given in Table VIII; fractional atomic coordinates are listed in Tables IX–XIII. X-ray data were collected on Nicolet P3 (**4**, **19**) and Syntex P2$_1$ (**20**, **23**) diffractometers, which are each equipped with modified LT-2 and LT-1 low-temperature systems, respectively. Laue symmetry determination, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described techniques.[33]

All data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale. The systematic extinctions observed for **4** and **19** were $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$; the diffraction symmetry was $2/m$. The centrosymmetric monoclinic space group, $P2_1/n$, a nonstandard setting of $P2_1/c$ [C^5_{2h}; No 14] was uniquely defined. The systematic extinctions observed for **20** were hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$; the diffraction symmetry was $2/m$. The two possible monoclinic space groups are Cc [C^4_s; No. 9] or $C2/c$ [C^6_{2h}; No. 15]. The latter centrosymmetric space group was chosen and later shown to be the correct choice. There were no systematic extinctions or any diffraction symmetry other than the Friedel condition observed for **23**. The two possible triclinic space groups are the noncentrosymmetric $P1$ [C^1_1; No. 1] or the centrosymmetric $P\bar{1}$ [C^1_i; No. 2]. With $Z = 2$ and no expectation of a resolved chiral molecule, the latter centrosymmetric space group is far more probable and was later shown to be the correct choice by the successful refinement in $P\bar{1}$.

All crystallographic calculations were carried out by using either the UCI modified version of the UCLA Crystallographic Computing Package[34] or the SHELXTL PLUS program set.[35] The analytical scattering factors for neutral atoms were used through the analysis;[36] the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[37] were included.

The structures were solved by direct methods (SHELXTL PLUS) and refined by full least-squares methods. There is a methylene chloride solvent molecule of crystallization present in the lattice of **20**. The carbon atom lies on a 2-fold rotation axis at 0, y, $^1/_4$; thus there is $^1/_2$CH$_2$Cl$_2$ per formula unit. Hydrogen atom contributions were either included by using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2 (**16**, **20**) or located from a difference-Fourier map and refined isotropically (**4**, **19**, **23**). Refinement of positional and anisotropic thermal parameters led to convergence (see Table VIII).

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Supplementary Material Available: Listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters (23 pages); tables of calculated and observed structure factors (64 pages). Ordering information is given on any current masthead page.

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