

= 1.5418 Å) radiation in $W-2\theta$ scan mode with $\Delta\omega = (1.0 + 0.14 \tan \theta)$ and aperture width of $(3 + 0.42 \tan \theta)$. Structures were solved by employing direct methods and calculations were performed on a VAX 11/730 computing system using the SDP package.²⁸ The packing of both the molecules **16** and **23** is stabilized by van der Waals interactions.

Computational Details

The constrained-synchronous transition-state structure for the ethylene + butadiene cycloaddition computed at the MNDO level was chosen as the basic model.²⁶ The optimized MNDO geometries of NPBQ and DNPBQ were then grafted onto this structure by appropriate replacement of the hydrogen atoms in the ethylene unit. The different dienes studied experimentally were represented by the following three models: 1,3-butadiene, *o*-quinodimethane, and 2,3-dichlorobutadiene. The geometrical modifications to the diene part of the transition-state model was carried out as for the diene with MNDO or standard geometries. The steric interactions between the diene and the norbornyl skeleton of the dienophile were computed by using MM2 parameters.²³ Since torsional

effects were not likely to be important in the present systems, only the van der Waals interactions were considered. Therefore, unlike the earlier study,¹¹ no partial geometry optimization was carried out. There was also no need to add new parameters to the MM2 force field. The various transition-state model geometries for the top and the bottom face attack in each case as well as the computed nonbonded interaction energies are included as supplementary material.

Acknowledgment. S.P. and A.P. thank the CSIR, New Delhi, for the award of a Research Fellowship. Research at Hyderabad was supported through UGC Special Assistance and COSIST programs. We thank Mr. Srinivas Rao Karra and Mr. S. Sanyanarayana for their help in the preparation of some compounds and for recording NMR spectra, respectively.

Supplementary Material Available: Tables of optimized MNDO geometries and heats of formation of **3** and **4**, the transition-state model geometries with **3** and **4** as the dienophile and butadiene, *o*-quinodimethane, and 2,3-dichlorobutadiene as the diene for both the top and the bottom face cycloadditions, along with the computed nonbonded interaction energies (14 pages). Ordering information is given on any current masthead page.

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π -Bonding in Four-Coordinate Aluminum Aryloxy Compounds

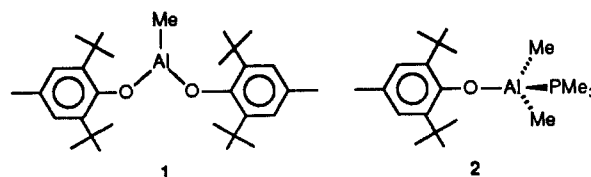
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Abstract: The interaction of AlMe_3 with the substituted phenols 2,6-di-*tert*-butyl-4-methylphenol (BHT-H), 2,6-diisopropylphenol (DIP-H), and 2,4,6-trimethylphenol (MesOH) in the presence of pyridine (py) or 3,5-dimethylpyridine (3,5-Me₂py) leads to the formation of mono, bis, and tris aryloxy compounds. The molecular structures of $\text{AlMe}_2(\text{BHT})(\text{py})$ (**3a**), $\text{AlMe}(\text{OMes})_2(3,5\text{-Me}_2\text{py})$ (**8b**), and $\text{Al}(\text{DIP})_3(\text{py})$ (**7a**) have been determined by X-ray crystallography. The Al–O distances are shorter and Al–O–C angles larger than usually found for aluminum alkoxides. The presence of a π -type interaction between the aryloxy ligands and the four-coordinate aluminum centers is proposed to account for the structural results. Compound **3a**: monoclinic $P2_1/n$, $a = 10.193$ (7) Å, $b = 17.989$ (10) Å, $c = 12.249$ (11) Å, $\beta = 96.44$ (6)°, $Z = 4$, $R = 0.076$, $R_w = 0.078$. Compound **8b**: monoclinic $P2_1/n$, $a = 11.767$ (2) Å, $b = 10.232$ (2) Å, $c = 21.562$ (5) Å, $\beta = 105.43$ (2)°, $Z = 4$, $R = 0.076$, $R_w = 0.091$. Compound **7a**: monoclinic $P2_1/n$, $a = 13.032$ (2) Å, $b = 21.308$ (3) Å, $c = 14.605$ (2) Å, $\beta = 107.99$ (1)°, $Z = 4$, $R = 0.068$, $R_w = 0.068$.

The tendency of aluminum alkoxide and aryloxy compounds to maximize their coordination number by associating to give aggregates containing tetrahedral and octahedral centers is well-documented.¹ The use, however, of the sterically hindered aryloxy derived from 2,6-di-*tert*-butyl-4-methylphenol (BHT-H, from the trivial name butylated hydroxytoluene) results in the isolation of monomeric aryloxy compounds of aluminum.^{2,3} The X-ray structural determination of $\text{AlMe}(\text{BHT})_2$ (**1**) has been reported,⁴ and it confirms the monomeric nature of this compound. The short Al–O distances [average 1.686 (2) Å] and large Al–O–C angles [average 143.6 (2)°] in **1** are consistent with the presence of π -bonding between the aryloxy oxygens and the vacant aluminum p_z orbital (z perpendicular to the AlO_2C plane). This bonding scheme is compatible with the commonly accepted concept that the presence of π -bonding to a group III element requires a trigonal planar coordinatively unsaturated metal center. We have recently reported, however, that π -bonding may also be

present between oxygen and aluminum in four-coordinate complexes.⁵



The presence of a short Al–O distance [1.736 (5) Å] and a large Al–O–C angle [164.5 (4)°] in the X-ray structure of AlMe_2 -

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

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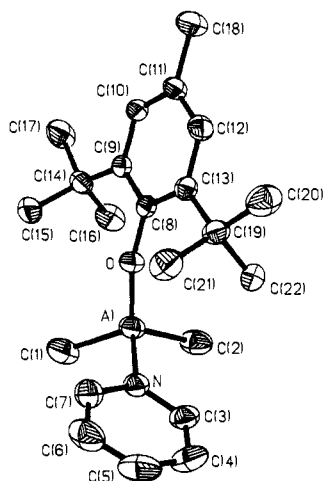


Figure 1. The structure of $\text{AlMe}_2(\text{BHT})(\text{py})$ (**3a**). Thermal ellipsoids are drawn at the 30% level and hydrogen atoms are omitted for clarity.

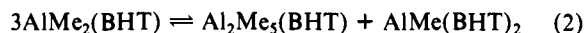
(BHT) PMe_3 (**2**),⁵ where neither a vacant aluminum p orbital nor an energetically accessible aluminum d orbital is available for π -bonding, led to our proposal that π -donation from the oxygen lone pair orbitals to the Al-C and Al-P σ antibonding orbitals is present. The gas-phase photoelectron spectrum of **2** supports π -donation from an oxygen p orbital of the phenoxide ligand into the Al-P σ^* orbital.⁶

In an attempt to further explore this chemistry we have studied the use of less sterically demanding phenoxides. We have found, however, that phosphines are not sufficiently basic to cleave the aryloxy bridged dimers presumably formed on the addition of phenols to AlMe_3 .⁷ We have therefore investigated the use of pyridine (py) and 3,5-dimethylpyridine (3,5-Me₂py) as Lewis bases.

We report here the synthesis and structural characterization of a series of monomeric, four-coordinate aluminum aryloxy compounds, $\text{AlMe}_{3-x}(\text{OR})_x\text{L}$ ($x = 1, 2, 3$; L = py, 3,5-Me₂py). The structures of these compounds are consistent with the presence of π -bonding between oxygen and the four-coordinate aluminum center.

Results and Discussion

Addition of 1 equiv of py to an equimolar mixture of AlMe_3 and BHT-H in pentane at room temperature results, after the removal of all volatiles, in the formation of $\text{AlMe}_2(\text{BHT})\text{py}$ (**3a**) and $\text{AlMe}(\text{BHT})_2\text{py}$ (**4a**), in a 7:3 ratio. A recent NMR study by Ittel et al.⁴ of the species present in an equimolar solution of AlMe_3 and BHT-H showed that two disproportionations occur in solution (eqs 1 and 2).



The formation of a mixture of **3a** and **4a** is in contrast to the analogous reaction with PMe_3 , where $\text{AlMe}_2(\text{BHT})\text{PMe}_3$ is the only isolated product.⁵ This difference is indicative of the reduced basicity and increased steric bulk of PMe_3 as compared with py. Compound **3a** is isolated in pure form by sublimation from the mixture; **4a** is best prepared directly by the reaction of **1** with py. Recrystallization of **3a** or **4a** can be accomplished without disproportionation.

Attempts to carry out similar reactions with the less sterically demanding 2,6-diisopropylphenol (DIP-H) resulted in the formation of an inseparable mixture of $\text{AlMe}_2(\text{DIP})\text{py}$ (**5a**) and $\text{AlMe}(\text{DIP})_2\text{py}$ (**6a**). Interaction of AlMe_3 with 3 equiv of DIP-H in pentane followed by the addition of an excess of py results in

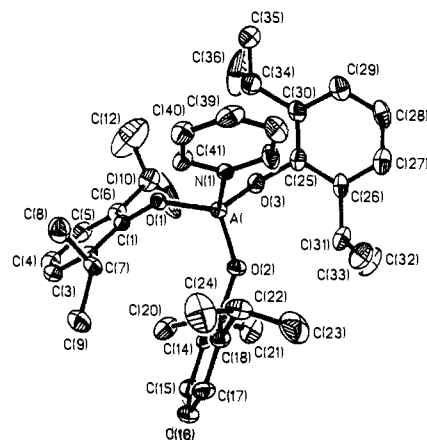


Figure 2. The structure of $\text{Al}(\text{DIP})_3\text{py}$ (**7a**). Thermal ellipsoids are drawn at the 30% level and hydrogen atoms are omitted for clarity.

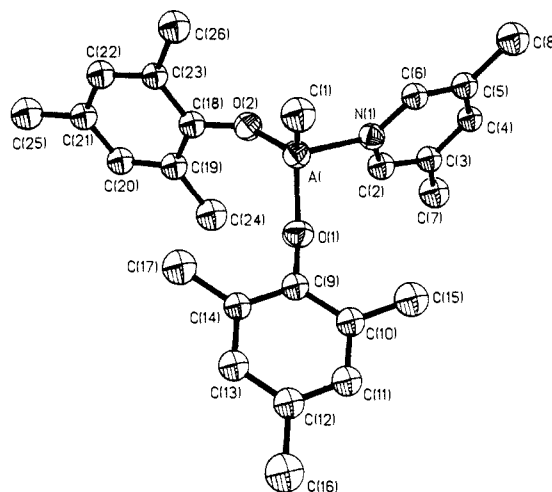


Figure 3. The structure of $\text{AlMe}(\text{OMe})_2(3,5\text{-Me}_2\text{py})$ (**8b**). Thermal ellipsoids are drawn at the 30% level and hydrogen atoms are omitted for clarity.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) in $\text{AlMe}_2(\text{BHT})(\text{py})$

Al(1)–O(1)	1.740 (4)	Al(1)–N(1)	1.993 (5)
Al(1)–C(1)	1.964 (6)	Al(1)–C(2)	1.956 (6)
O(1)–C(8)	1.357 (5)		
O(1)–Al(1)–N(1)	101.3 (2)	O(1)–Al(1)–C(1)	116.8 (2)
N(1)–Al(1)–C(1)	100.0 (2)	O(1)–Al(1)–C(2)	115.5 (2)
N(1)–Al(1)–C(2)	105.9 (2)	C(1)–Al(1)–C(2)	114.3 (3)
Al(1)–O(1)–C(8)	156.1 (3)		

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) in $\text{Al}(\text{DIP})_3(\text{py})$

Al(1)–O(1)	1.711 (3)	Al(1)–O(2)	1.702 (4)
Al(1)–O(3)	1.702 (3)	Al(1)–N(1)	1.957 (3)
O(1)–C(1)	1.369 (5)	O(2)–C(13)	1.361 (6)
O(1)–Al(1)–O(2)	116.7 (2)	O(1)–Al(1)–O(3)	114.6 (2)
O(2)–Al(1)–O(3)	112.4 (2)	O(1)–Al(1)–N(1)	100.8 (2)
O(2)–Al(1)–N(1)	105.2 (2)	O(3)–Al(1)–N(1)	105.2 (2)
Al(1)–O(1)–C(1)	141.1 (3)	Al(1)–O(2)–C(13)	143.8 (3)
Al(1)–O(3)–C(25)	143.2 (3)	Al(1)–N(1)–C(37)	123.8 (3)
Al(1)–N(1)–C(41)	119.1 (3)		

the isolation of $\text{Al}(\text{DIP})_3\text{py}$ (**7a**). It should be noted that attempts to prepare $\text{Al}(\text{BHT})_3$ have been unsuccessful. Further reduction in the steric bulk of the phenoxy ligand to 2,4,6-trimethylphenol (MesOH) allows the isolation of both $\text{AlMe}(\text{OMe})_2\text{py}$ (**8a**) and $\text{Al}(\text{OMe})_3\text{py}$ (**9a**).

The 3,5-Me₂py complexes (**3b–5b**, **7b–9b**) can be prepared by analogous routes. Compound **6b** can be separated from **7b** by repeated fractional crystallization. All new compounds have been

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Table III. Selected Bond Lengths (Å) and Bond Angles (deg) in $\text{AlMe}(\text{OMe})_2(3,5\text{-Me}_2\text{py})$

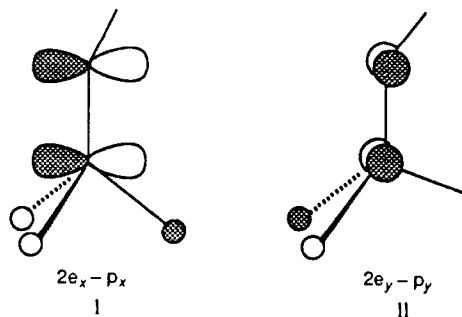
Al(1)–O(1)	1.722 (7)	Al(1)–O(2)	1.714 (6)
Al(1)–N(1)	1.961 (7)	Al(1)–C(1)	1.946 (10)
O(1)–C(9)	1.356 (11)	O(2)–C(18)	1.356 (11)
O(1)–Al(1)–O(2)	111.1 (3)	O(1)–Al(1)–N(1)	100.6 (3)
O(2)–Al(1)–N(1)	98.3 (3)	O(1)–Al(1)–C(1)	115.5 (4)
O(2)–Al(1)–C(1)	118.7 (4)	N(1)–Al(1)–C(1)	109.4 (4)
Al(1)–O(1)–C(9)	140.6 (6)	Al(1)–O(2)–C(18)	145.8 (6)

fully characterized by IR and ^1H and ^{13}C NMR spectroscopy.

The molecular structures of **3a**, **7a**, and **8b** have been determined by X-ray crystallography and are shown in Figures 1, 2, and 3, respectively. Selected bond lengths and angles are given in Tables 1–111. The structures consist of discrete monomeric units. As was observed for the structure of $\text{AlMe}_2(\text{BHT}) (\text{PMe}_3)$,⁶ the geometry around each aluminum is highly distorted from tetrahedral, with the angles associated with the pyridine ligands being the most acute. The similarity in aluminum coordination geometries in these compounds is illustrated by comparing the sums of interligand angles not associated with the pyridine nitrogen [$346.6 (7)^\circ$ (**3a**), $345.3 (10)^\circ$ (**8b**), and $343.7 (6)^\circ$ (**7a**)]. The similarity in the geometry around the aluminum is surprising in view of the vastly different steric requirements expected for the different number of phenoxide ligands and the range of substituents on the phenoxide.

The Al–C bonds in **3a** [1.956 (6), 1.964 (6) Å] and **8b** [1.946 (10) Å] are in the range observed previously for aluminum–methyl compounds (1.90–2.01 Å).⁸ The Al–N bond distances are within the range previously reported for aluminum–nitrogen bonds (1.88–2.09 Å).⁹ It is noteworthy, however, that the Al–N bond in **3a** [1.993 (5) Å] is slightly longer than that found in **8b** [1.961 (7) Å] and **7a** [1.957 (3) Å], in accord with Lewis acidity and the opposite of what would be expected if steric effects predominated.

In the structure of **3a**, **7a**, and **8b** the Al–O–C angles [$140.6 (6)$ – $156.1 (3)^\circ$] are much larger than usually observed for main-group alkoxides, although they are in the range found for those transition-metal alkoxide complexes where significant $\text{p}\pi\text{-d}\pi$ bonding is present.¹⁰ In addition the Al–O distances [1.702 (4)–1.740 (4) Å] are short compared to the normal range¹¹ of 1.8–2.0 Å. We have previously proposed⁵ that the short Al–O distance and large Al–O–C angle found in the structure of $\text{AlMe}_2(\text{BHT}) (\text{PMe}_3)$ were due primarily to π -donation from the oxygen lone pair, p_z , perpendicular to the phenoxide ring into the π -acceptor σ -antibonding molecular orbital, $2e_x$ (I).¹² This proposal has been confirmed by gas-phase photoelectron spectroscopy.⁶



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The orientation of the phenoxide ring in **3a** is essentially the same as that in **2**. The Al–O distance [1.740 (4) Å] is comparable to that in **2** [1.736 (5) Å]; however, the Al–O–C angle is more acute, $156.1 (3)^\circ$, suggesting a reduced π -interaction from the aryloxide ligand. The reduction in the Al–O–C angle between **2** and **3a** may be due to the larger electron donor ability of pyridine, as compared with PMe_3 , which would regulate the effective π -donation of the aryloxide. Alternatively, the $2e_x\text{-}p_x$ orbital overlap (I), which presumably has the greatest influence over the bond angle, is greater when the $2e_x$ orbital is primarily Al–P σ^* , as in **2**, rather than Al–C σ^* , as in **3a**. Despite the decrease in Al–O–C angle between **2** and **3a** it is clear from the short Al–O distance that the presence of π -bonding is nearly independent of the ligands around aluminum.

The Al–O distances in **7a** and **8b** [1.702 (4)–1.722 (4) Å] are comparable to those for the monoaryloxide compounds, **3a**. The Al–O–C angle, however, is reduced for **7a** and **8b** [$140.6 (6)$ – $145.8 (6)^\circ$], suggesting a reduction in π -bonding. It should be noted that the Al–O–C bond angles in **7a** and **8b** are similar to those found for **1**,⁴ the structure of which is consistent with π -bonding between the lone pairs co-planar with the aromatic ring on each alkoxide, and the vacant p_z orbital on aluminum.

The Al–O–C angle would be more dependent on the magnitude of π -donation from the lone pair perpendicular to the phenoxide ring, p_z (I), rather than the lone pair parallel, p_y (II), to the phenoxide ring. It is unlikely, however, that the Al–O distance would vary significantly between either form of π -bonding.

If in **7a** and **8b** only one oxygen lone pair on each aryloxide is involved in π -bonding, as in **1**, then the aryloxide ligand would orient so as to attain a maximum orbital overlap between the oxygen p -orbital type lone pair and the Al–X σ^* orbitals. The orientation of one aryloxide (O1) in **8b** is such that one of the oxygen lone pairs is suitable for donation into the Al–N σ^* orbital. The second aryloxide (O2) is oriented for π -donation into the Al–O1 σ^* orbital. Two of the aryloxides in **7a** are oriented in a similar fashion to those in **8b** with the third aryloxide (O1) oriented for π -donation into the Al–O3 σ^* orbital.

The Al–O–C angles in **7a** and **8b** [$140.6 (6)$ – $145.8 (6)^\circ$] are most probably due primarily to the interaction between the aryl π^* orbital and the lone pair perpendicular to the aryl ring. Such an interaction has been used to explain the large Si–O–C angles present in silicon aryloxides where no π -interaction is observed between the oxygen and silicon.¹³

If π -donation is present from the aryloxide oxygen to the four-coordinate aluminum center, then ^{27}Al NMR should be a useful technique to augment X-ray crystallographic data. The ^{27}Al NMR shifts of the aryloxide compounds cover a wide range, δ 140–47 ppm. Within this range, however, there are three distinct groups: the mono aryloxide δ 134–140 ppm; the bis aryloxides δ 69–72 ppm; and the tris aryloxides δ 47–50 ppm. The upfield shift of the ^{27}Al NMR signal with the substitution of a methyl group by an aryloxide is counter intuitive based on the relative electronegativity of the substituents. This trend is consistent, however, with the presence of π -donation of electron density onto the aluminum. The similarity in the ^{27}Al NMR shifts for **7a** (δ 48 ppm) and **9a** (δ 50 ppm) is an indication that the steric hindrance at the ortho position on the phenol rings has little effect on the aluminum center.

In conclusion all spectroscopic and structural results for these systems are consistent with π -bonding between the aryloxide ligands and four-coordinate aluminum centers involving an overlap between the Al–X σ^* and the oxygen lone pairs.

Experimental Section

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Melting points were determined in sealed capillaries and are uncorrected. IR spectra ($4000\text{--}700\text{ cm}^{-1}$) were recorded on a Perkin-Elmer 137 grating spectrometer as Nujol mulls. NMR spectra, in C_6D_6 , were recorded on Bruker AM-250 (^1H), Bruker AM-500 (^{13}C), and Varian 300 (^{27}Al) spectrometers [δ in parts per million relative to

(13) (a) Bordeau, M.; Dédier, J.; Frainnet, É. *J. Organomet. Chem.* **1973**, *61*, 91. (b) Healy, M. D.; Barron, A. R. *J. Organomet. Chem.* **1990**, *381*, 165.

Table IV. Summary of X-ray Diffraction Data

compd	AlMe ₂ (BHT)(py) (3a)	AlMe(OMe) ₂ (3,5-Me ₂ py) (8b)	Al(DIP) ₃ (py) (7a)
empirical formula	C ₂₂ H ₃₄ NOAl	C ₂₆ H ₃₄ NO ₂ Al	C ₄₁ H ₅₆ NO ₃ Al
cryst size, mm	0.30 × 0.60 × 0.70	0.33 × 0.36 × 0.40	0.20 × 0.50 × 0.57
cryst system	monoclinic	monoclinic	monoclinic
space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n
a, Å	10.193 (7)	11.767 (2)	13.032 (2)
b, Å	17.989 (10)	10.232 (2)	21.308 (3)
c, Å	12.249 (11)	21.562 (5)	14.605 (2)
β, deg	96.44 (6)	105.43 (2)	107.99 (1)
vol, Å ³	2232 (3)	2502.5 (9)	3875.3 (11)
Z	4	4	4
density (calcd), mg/m ³	1.058	1.113	1.098
abs coeff, mm ⁻¹	0.095	0.097	0.084
radiation	Mo Kα (λ = 0.71073 Å)	graphite, monochromator	
temp, K	296	296	183
2θ range, deg	4.0 to 45.0	4.0 to 40.0	4.0 to 45.0
scan type	θ-2θ	ω	θ-2θ
index ranges	0 ≤ h ≤ 10, 0 ≤ k ≤ 19, -13 ≤ l ≤ 12	0 ≤ h ≤ 11, 0 ≤ k ≤ 9, -20 ≤ l ≤ 20	0 ≤ h ≤ 14, 0 ≤ k ≤ 22, -15 ≤ l ≤ 14
reflcs collected	3256	2480	5489
independent reflcs	2518	2038	4433
obsd reflcs	1967 (F _o > 3.0σ F _o)	1285 (F _o > 5.0σ F _o)	3175 (F _o > 4.0σ F _o)
weighting scheme	w ⁻¹ = σ ² (F _o) + 0.0008(F _o) ²	w ⁻¹ = σ ² (F _o) + 0.0007(F _o) ²	w ⁻¹ = σ ² (F _o) + 0.0004(F _o) ²
final R indices (obsd data)	R = 0.076, R _w = 0.078	R = 0.076, R _w = 0.091	R = 0.068, R _w = 0.068
goodness of fit	1.69	2.17	1.91
largest diff peak, eÅ ⁻³	0.21	0.35	0.50

SiMe₄ (¹H and ¹³C) and Al(H₂O)₆³⁺ (²⁷Al)]. All manipulations were carried out under nitrogen. Solvents were dried, distilled, and degassed prior to use.

2,6-Di-*tert*-butyl-4-methylphenol (BHT-H), 2,4,6-trimethylphenol (MesOH), and 2,6-diisopropylphenol (DIP-H) (Aldrich) were sublimed prior to use. Trimethylaluminum (2.0 M solution in hexane) was used as supplied (Aldrich). Pyridine and 3,5-dimethylpyridine (Aldrich) were distilled prior to use and stored over molecular sieves. AlMe(BHT)₂ was prepared as previously described.⁵

AlMe₂(BHT)py (3a). To a solution of BHT-H (2.00 g, 9.1 mmol) in pentane (60 mL) was added AlMe₃ in hexane (4.5 mL, 9.1 mmol). After the solution was stirred for 4 h, py (0.75 mL, 9.23 mmol) was added. The resulting solution was stirred for 2 h and reduced to dryness under vacuum. Sublimation of the residue (170 °C) under vacuum gave colorless crystals: yield 1.78 g, 55%; mp 169–172 °C; IR 1615 (m), 1425 (s), 1288 (sh), 1284 (s), 1230 (m), 1195 (s), 1175 (w), 1138 (w), 1080 (s), 1065 (m), 1035 (m), 965 (w), 935 (w), 900 (sh), 882 (s), 820 (w), 812 (sh), 792 (w), 772 (w) cm⁻¹; ¹H NMR 8.20 (2 H, d, J(H-H) = 6.2 Hz, *o*-H, py), 7.27 (2 H, s, *m*-H, BHT), 6.68 (1 H, d, J(H-H) = 6.3 Hz, *p*-H, py), 6.30 (2 H, dd, J(H-H) = 6.3 Hz, *m*-H, py), 2.35 (3 H, s, CH₃, BHT), 1.51 (18 H, s, CCH₃, BHT), -0.09 (6 H, s, AlCH₃); ¹³C NMR 155.6 [(OC)], 147.4 (*o*-C, py), 140.2 (*p*-C, py), 138.7 (*o*-C, BHT), 126.2 (*m*-C, BHT), 125.4 (*p*-C, BHT), 124.9 (*m*-C, py), 35.1 [C(CH₃)₃, BHT], 31.4 [C(CH₃)₃, BHT], 21.6 (CH₃, BHT), -5.10 (AlCH₃); ²⁷Al NMR 134 (W_{1/2} = 6320 Hz). Anal. Calcd for C₂₂H₃₄AlNO: C, 74.32; H, 9.64; N, 3.94. Found: C, 73.73; H, 9.64; N, 3.70.

AlMe₂(BHT)(3,5-Me₂py) (3b). The synthesis was carried out in an analogous manner to that of 3a with BHT-H (1.50 g, 6.82 mmol), AlMe₃ (3.40 mL, 6.80 mmol), and 3,5-Me₂py (0.78 mL, 6.84 mmol). ¹H NMR of the crude reaction mixture indicated that the major impurity was AlMe₃(3,5-Me₂py). Separation was carried out by sublimation, with AlMe₃(3,5-Me₂py) subliming in vacuo at 80 °C and 3b subliming as crystalline material at 160–162 °C: yield 2.34 g, 89%; mp 151–153 °C; IR 1775 (w), 1625 (m), 1435 (s), 1375 (s), 1290 (s), 1245 (sh), 1205 (s), 1170 (s), 1140 (m), 1090 (w), 1060 (m), 1040 (w), 965 (br, w), 940 (w), 905 (sh), 880 (s), 823 (w), 793 (s), 718 (s) cm⁻¹; ¹H NMR 8.18 (2 H, s, *o*-H, lut), 7.29 (2 H, s, *m*-H, BHT), 6.38 (1 H, s, *p*-H, lut), 2.37 (3 H, s, C₆H₂CH₃), 1.57 (18 H, s, CCH₃, BHT), 1.46 (6 H, s, CH₃, lut), 0.04 (6 H, s, Al-CH₃); ¹³C NMR 155.8 (OC, BHT), 144.9 (*o*-C, lut), 141.8 (*p*-C, lut), 138.7 (*o*-C, BHT), 135.1 (*m*-C, lut), 126.1 (*m*-C, BHT), 125.2 (*p*-C, BHT), 35.0 [C(CH₃)₃, BHT], 31.3 [C(CH₃)₃, BHT], 21.5 (CH₃, BHT), 17.5 (CH₃, lut), -5.21 (AlCH₃). ²⁷Al NMR 134 (W_{1/2} = 6300 Hz). Anal. Calcd for C₂₂H₃₈AlNO: C, 75.15; H, 9.99; N, 3.65. Found: C, 75.25; H, 9.88; N, 3.60.

AlMe(BHT)₂(py) (4a). Py (1.0 mL, 12.3 mmol) was added to a pentane (40 mL) solution of AlMe(BHT)₂ (1.0 g, 2.1 mmol) and the resulting mixture stirred for 8 h. Removal of the solvent in vacuo gave a white powder that was recrystallized from pentane/benzene: yield 1.1 g, 94%; mp 178–180 °C dec; IR 1640 (m), 1430 (s), 1380 (sh), 1280 (s), 1233 (s), 1220 (sh), 1180 (w), 1143 (m), 1090 (s), 1070 (m), 1040 (m), 970 (w), 938 (w), 900 (s), 890 (sh), 885 (sh), 872 (m), 825 (w), 790 (m),

775 (w), 737 (w), 705 (s); ¹H NMR 8.43 (2 H, d, J(H-H) = 6.8 Hz, *o*-H, py), 7.22 (4 H, s, *m*-H, BHT), 6.61 (1 H, t, J(H-H) = 6.8 Hz, *p*-H, py), 6.22 (2 H, dd, J(H-H) = 6.8 Hz, *o*-H, py), 2.32 (6 H, s, CH₃, BHT), 1.46 (36 H, s, CCH₃, BHT), 0.23 (3 H, s, AlCH₃); ¹³C NMR 155.6 (*o*-C, BHT), 148.4 (*m*-C, py), 141.0 (*p*-C, py), 138.5 (*o*-C, BHT), 126.4 (*m*-C, BHT), 125.8 (*p*-C, BHT), 124.8 (*m*-C, py), 35.3 [C(CH₃)₃, BHT], 31.8 [C(CH₃)₃, BHT], 21.3 (CH₃, BHT), -2.1 (AlCH₃); ²⁷Al NMR 72 (W_{1/2} = 6390 Hz). Anal. Calcd for C₃₆H₅₄AlNO₂: C, 77.29; H, 9.73; N, 2.50. Found: C, 77.41; H, 9.70; N, 2.49.

AlMe(BHT)₂(3,5-Me₂py) (4b). The synthesis was carried out in an analogous manner to that of 4a with AlMe(BHT)₂ (1.68 g, 3.5 mmol) and 0.4 mL, 3.5 mmol): yield 1.9 g, 95%; mp 171–174 °C; IR 1625 (w), 1435 (s), 1290 (sh), 1266 (s), 1234 (sh), 1214 (m), 1164 (s), 1138 (m), 1055 (m), 1040 (m), 990 (w), 970 (w), 956 (w), 940 (w), 895 (s), 875 (s), 823 (w), 797 (w), 785 (m), 735 (m), 722 (s), 716 (sh), 702 (m) cm⁻¹; ¹H NMR 8.31 (2 H, s, *o*-H, lut), 7.21 (4 H, s, *m*-H, BHT), 6.43 (1 H, s, *p*-H, lut), 2.31 (6 H, s, *p*-H, lut), 1.51 (6 H, s, CH₃, lut), 1.50 [36 H, s, C(CH₃)₃, BHT], 0.30 (3 H, s, AlCH₃); ¹³C NMR 155.8 (OC, BHT), 145.9 (*o*-C, lut), 142.4 (*p*-CH, lut), 138.5 (*o*-C, BHT), 135.0 (*m*-C, lut), 126.3 (*m*-C, BHT), 125.6 (*p*-C, BHT), 35.3 [C(CH₃)₃, BHT], 31.8 [C(CH₃)₃, BHT], 21.3 (CH₃, BHT), 17.5 (*m*-CH₃, lut), -2.3 (AlCH₃); ²⁷Al NMR 69 (W_{1/2} = 7428 Hz). Anal. Calcd for C₃₈H₅₈AlN₂O₂: C, 77.69; H, 9.95; N, 2.38. Found: C, 77.39; H, 9.94; N, 2.22.

Attempted Synthesis of AlMe(DIP)₂(py) (6a). To a stirred pentane (40 mL) solution of DIP-H (1.00 g, 5.61 mmol) at room temperature was added AlMe₃ in hexane (1.4 mL, 2.8 mmol) via syringe. After 0.5 h py (1.0 mL, 12.3 mmol) was added and the resulting solution stirred for 8 h. Removal of the solvent and excess pyridine under vacuum yielded a white powder, the ¹H NMR spectra of which indicate a mixture of products. Attempts to purify by fractional crystallization and vacuum sublimation were unsuccessful. Repeating the reaction in toluene also resulted in a mixture. The impurities are Al(DIP)₃(bpy) (7a) and presumably AlMe₂(DIP)py (5a). Reaction of the appropriate ratio of AlMe₃, DIP-H, and py to form 5a results in a similar mixture.

AlMe(DIP)₂(3,5-Me₂py) (6b). With use of reaction conditions analogous to those for 6a, with DIP-H (1.0 g, 5.6 mmol), AlMe₃ (1.4 mL, 2.8 mmol), and 3,5-Me₂py (0.32 mL, 2.8 mmol), crystallization from pentane/toluene resulted in the formation of crystals of two different forms. One set gave the ¹H and ¹³C NMR of 7b, and the other set analyzed for 6b. Repeated recrystallization resulted in the separation of 7b and 6b: mp 90–92 °C; IR 1610 (m), 1585 (m), 1350 (s), 1283 (s), 1225 (s), 1218 (sh), 1188 (w), 1162 (s), 1138 (m), 1113 (m), 1070 (sh), 1060 (s), 935 (s), 921 (s), 896 (m), 883 (m), 805 (s), 768 (s), 735 (s), 712 (m) cm⁻¹; ¹H NMR 8.32 (2 H, s, *o*-H, lut), 7.17 [4 H, d, J(H-H) = 7.5 Hz, *m*-H, DIP], 6.95 [2 H, t, J(H-H) = 7.5 Hz, *p*-H, DIP], 6.51 (1 H, s, *p*-H, lut), 3.55 [4 H, p, J(H-H) = 6.8 Hz, CH(CH₃)₂, DIP], 1.56 (6 H, s, CH₃, lut), 1.19 [24 H, d, J(H-H) = 6.8 Hz, CH(CH₃)₂, DIP], 0.02 (3 H, s, AlCH₃). ¹³C NMR 153.6 (OC, DIP), 144.6 (*o*-C, lut), 142.5 (*p*-C, lut), 137.3 (*m*-C, lut), 135.5 (*o*-C, DIP), 123.3 (*m*-C, DIP), 119.1 (*p*-C, DIP), 27.3 [CH(CH₃)₂, DIP], 23.7 [CH(CH₃)₂, DIP], 17.6 [CH₃, lut], -11.0 (AlCH₃).

Table V. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3 \text{ \AA}^2$) of the Non-Hydrogen Atoms in $\text{AlMe}_2(\text{BHT})(\text{py})$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Al(1)	556 (2)	2058 (1)	4098 (1)	64 (1)
O(1)	-712 (3)	1422 (2)	3765 (2)	58 (1)
N(1)	1026 (4)	1847 (2)	5691 (4)	63 (2)
C(1)	2255 (5)	1843 (4)	3551 (4)	92 (3)
C(2)	39 (6)	3105 (3)	4003 (5)	88 (3)
C(3)	728 (5)	2293 (3)	6496 (5)	73 (2)
C(4)	1013 (6)	2122 (4)	7587 (5)	92 (3)
C(5)	1616 (7)	1471 (5)	7870 (6)	98 (3)
C(6)	1949 (6)	1009 (4)	7084 (7)	98 (3)
C(7)	1632 (6)	1209 (3)	6004 (5)	82 (3)
C(8)	-1894 (5)	1179 (2)	3273 (4)	47 (2)
C(9)	-2058 (4)	1013 (2)	2135 (4)	48 (2)
C(10)	-3291 (5)	768 (2)	1677 (4)	52 (2)
C(11)	-4345 (5)	666 (3)	2264 (4)	55 (2)
C(12)	-4163 (5)	824 (3)	3372 (4)	58 (2)
C(13)	-2953 (5)	1068 (2)	3915 (4)	51 (2)
C(14)	-942 (5)	1090 (3)	1415 (4)	62 (2)
C(15)	243 (5)	604 (3)	1857 (4)	83 (2)
C(16)	-569 (5)	1918 (3)	1329 (4)	83 (2)
C(17)	-1335 (5)	833 (4)	228 (4)	92 (3)
C(18)	-5667 (5)	406 (3)	1709 (4)	80 (2)
C(19)	-2835 (5)	1207 (3)	5157 (4)	60 (2)
C(20)	-4133 (6)	1059 (3)	5658 (4)	90 (3)
C(21)	-1769 (6)	703 (3)	5743 (4)	81 (2)
C(22)	-2526 (5)	2030 (3)	5395 (4)	69 (2)

^aEquivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Al(DIP)₃(py) (7a). To a solution of DIP-H (1.0 g, 5.6 mmol) in pentane (35 mL) at room temperature was added AlMe_3 in hexane (0.94 mL, 1.9 mmol). After the solution was stirred for 0.5 h, py (1.0 mL, 12.3 mmol) was added, and the resulting solution was stirred overnight and then reduced to dryness under vacuum. The resulting white powder was recrystallized from pentane/benzene to yield colorless crystals: yield 1.03 g, 85%; mp 199–202 °C; IR 1640 (w), 1605 (w), 1380 (sh), 1350 (s), 1290 (s), 1235 (s), 1185 (w), 1140 (w), 1120 (m), 1090 (m), 1080 (m), 1065 (s), 1040 (w), 968 (sh), 940 (s), 895 (w), 812 (m), 768 (s), 750 (m), 710 (w) cm^{-1} ; ¹H NMR 8.50 [2 H, t, *J*(H–H) = 7.8 Hz, *o*-H, py], 7.14 (6 H, m, *m*-H, DIP), 6.98 (3 H, m, *p*-H, DIP), 6.60 [1 H, t, *J*(H–H) = 7.5 Hz, *p*-H, py], 6.22 (2 H, m, *m*-H, py), 3.54 [6 H, p, *J*(H–H) = 6.7 Hz, $\text{CH}(\text{CH}_3)_2$], 1.13 [36 H, d, *J*(H–H) = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$]; ¹³C NMR 152.4 (OC, DIP), 147.6 (*o*-C, py), 141.6 (*p*-C, py), 137.6 (*o*-C, DIP), 125.2 (*m*-C, py), 123.5 (*m*-C, DIP), 119.9 (*p*-C, DIP), 27.1 [$\text{CH}(\text{CH}_3)_2$, DIP], 23.8 [$\text{CH}(\text{CH}_3)_2$, DIP]; ²⁷Al NMR 48 ($W_{1/2}$ = 3095 Hz). Anal. Calcd for $\text{C}_{41}\text{H}_{56}\text{AlNO}$: C, 77.20; H, 8.85; N, 2.20. Found: C, 76.25; H, 8.73; N, 1.96.

Al(DIP)₃(3,5-Me₂py) (7b) was prepared in an analogous manner to **7a** with DIP-H (1.0 g, 5.6 mmol), AlMe_3 (0.94 mL, 1.9 mmol), and 3,5-Me₂py (0.3 mL, 2.6 mmol): yield 0.99 g, 79%; mp >260 °C; IR 1630 (m), 1600 (m), 1575 (w), 1345 (s), 1285 (s), 1225 (s), 1170 (s), 1130 (sh), 1112 (m), 1075 (sh), 1060 (s), 933 (vs), 893 (w), 882 (w), 818 (s), 810 (sh), 769 (s), 757 (s), 742 (sh), 712 (m); ¹H NMR 8.66 (2 H, s, *o*-H, lut), 7.18 (1 H, d, *J*(H–H) = 7.5 Hz, *p*-H, DIP), 6.98 (2 H, t, *J*(H–H) = 7.5 Hz, *m*-H, DIP), 6.50 (1 H, s, *p*-H, lut), 3.48 [6 H, d, *J*(H–H) = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$], 2.56 (6 H, s, CH_3 , py), 1.17 [36 H, d, *J*(H–H) = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$]; ¹³C NMR 152.6 (OC, DIP), 145.2 (*o*-C, lut), 143.0 (*p*-CH, lut), 137.6 (*o*-C, DIP), 135.7 (*m*-C, lut), 123.5 (*m*-C, DIP), 119.8 (*p*-C, DIP), 27.2 [$\text{CH}(\text{CH}_3)_2$, DIP], 23.9 [$\text{C}(\text{CH}_3)_2$, DIP], 17.5 (CH_3 , lut); ²⁷Al NMR 47 ($W_{1/2}$ = 3800). Anal. Calcd for $\text{C}_{43}\text{H}_{60}\text{AlNO}_3$: C, 77.55; H, 9.08; N, 2.10. Found: C, 76.89; H, 9.02; N, 1.77.

AlMe(OMes)₂(py) (8a). To a pentane solution of MesOH (0.40 g, 2.94 mmol) was added AlMe_3 (0.73 mL, 1.46 mmol) via syringe. The solution was stirred for 4 h; precipitation of a white solid occurred after 0.5 h. Py (0.20 mL, 2.46 mmol) was then added, dissolving the precipitate. After the solution was stirred for an additional 0.5 h, the solvent was reduced in volume until precipitation occurred. The solvent was removed from the precipitate via cannula and the resulting solid was dried in vacuo: yield 0.52 g, 91%; mp 129–131 °C dec; IR 1630 (m), 1325 (s), 1275 (s), 1233 (m), 1220 (w), 1180 (m), 1090 (s), 1070 (w), 1033 (w), 977 (m), 949 (w), 900 (s), 873 (s), 818 (w, br), 778 (m), 748 (m), 730 (w), 707 (s) cm^{-1} ; ¹H NMR 8.37 (2 H, d, *J*(H–H) = 4.9 Hz, *o*-H, py), 6.88 (6 H, *m*-H, Mes), 6.65 (1 H, t, *J*(H–H) = 4.9 Hz, *p*-H, py), 6.29 (2 H, t, *J*(H–H) = 4.9 Hz, *m*-H, py), 2.27 (18 H, s, *o*-CH₃, Mes), 2.24 (6 H, s, *p*-CH₃, Mes), -0.13 (3 H, s, AlCH_3); ¹³C NMR 154.2 (OC, Mes), 147.2 (*o*-C, py), 140.5 (*p*-C, py), 129.3 (*m*-C, Mes), 126.6 (*o*-C,

Table VI. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3 \text{ \AA}^2$) of the Non-Hydrogen Atoms in $\text{Al}(\text{DIP})_3\text{py}$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Al(1)	514 (1)	1551 (1)	8546 (1)	33 (1)
O(1)	-231 (2)	882 (1)	8480 (2)	35 (1)
O(2)	1404 (2)	1559 (1)	7903 (2)	40 (1)
O(3)	-206 (2)	2229 (1)	8425 (2)	47 (1)
N(1)	1407 (3)	1528 (2)	9897 (2)	34 (1)
C(1)	-771 (4)	437 (2)	7834 (3)	38 (2)
C(2)	-234 (4)	-106 (2)	7707 (3)	42 (2)
C(3)	-823 (5)	-560 (3)	7057 (4)	61 (3)
C(4)	-1891 (6)	-464 (3)	6552 (4)	64 (3)
C(5)	-2405 (5)	72 (3)	6684 (3)	58 (2)
C(6)	-1864 (4)	533 (2)	7324 (3)	46 (2)
C(7)	928 (4)	-216 (2)	8280 (4)	50 (2)
C(8)	1021 (5)	-578 (3)	9209 (4)	71 (3)
C(9)	1573 (5)	-552 (3)	7710 (4)	78 (3)
C(10)	-2435 (4)	1112 (3)	7492 (4)	59 (2)
C(11)	-3117 (9)	1418 (3)	6663 (6)	250 (8)
C(12)	-3076 (9)	1005 (5)	8082 (9)	339 (14)
C(13)	1818 (4)	1209 (2)	7322 (3)	36 (2)
C(14)	1194 (4)	1075 (2)	6376 (3)	40 (2)
C(15)	1653 (5)	729 (3)	5804 (4)	54 (2)
C(16)	2701 (5)	518 (2)	6145 (4)	59 (3)
C(17)	3315 (4)	653 (2)	7074 (4)	54 (2)
C(18)	2887 (4)	999 (2)	7684 (3)	43 (2)
C(19)	54 (2)	1323 (3)	5974 (3)	52 (2)
C(20)	-733 (4)	854 (3)	5333 (3)	72 (3)
C(21)	46 (5)	1934 (3)	5422 (4)	75 (3)
C(22)	3567 (4)	1153 (3)	8705 (3)	54 (2)
C(23)	4379 (6)	1659 (3)	8724 (5)	104 (4)
C(24)	4125 (6)	589 (3)	9253 (4)	109 (4)
C(25)	-165 (4)	2830 (2)	8757 (4)	45 (2)
C(26)	382 (4)	3285 (2)	8376 (4)	48 (2)
C(27)	409 (5)	3893 (3)	8717 (4)	64 (3)
C(28)	-78 (5)	4050 (3)	9388 (5)	69 (3)
C(29)	-626 (4)	3599 (3)	9746 (4)	65 (3)
C(30)	-668 (4)	2981 (2)	9433 (4)	52 (2)
C(31)	935 (4)	3126 (3)	7642 (4)	60 (2)
C(32)	660 (4)	3582 (3)	6783 (4)	85 (3)
C(33)	2153 (4)	3091 (3)	8089 (4)	74 (3)
C(34)	-1284 (5)	2496 (3)	9808 (5)	78 (3)
C(35)	-1011 (9)	2491 (3)	10859 (6)	173 (8)
C(36)	-2493 (6)	2587 (4)	9367 (9)	202 (8)
C(37)	1958 (4)	2022 (3)	10368 (4)	58 (2)
C(38)	2626 (5)	1983 (3)	11298 (4)	71 (3)
C(39)	2722 (4)	1420 (3)	11771 (4)	63 (3)
C(40)	2176 (4)	916 (3)	11305 (3)	59 (2)
C(41)	1529 (4)	985 (3)	10375 (3)	47 (2)

^aEquivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Mes), 126.3 (*p*-C, Mes), 125.0 (*m*-C, py), 20.7 (*p*-CH₃, Mes), 18.0 (*o*-CH₃, Mes), -11.0 (AlCH_3). Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{AlNO}_2$: C, 73.63; H, 7.73; N, 3.58. Found: C, 73.72; H, 7.79; N, 3.51.

AlMe(OMes)₂(3,5-Me₂py) (8b). To a pentane solution (30 mL) of MesOH (0.40 g, 2.94 mmol) was added via syringe AlMe_3 (0.73 mL, 1.46 mmol). After 20 min, 3,5-Me₂py (0.20 mL, 1.75 mmol) was added and the resulting solution stirred an additional 8 h. On removal of the solvent, a white powder was isolated, which was recrystallized from pentane/toluene: yield 0.23 g, 55%; mp 100–103 °C; IR 1620 (w), 1330 (s), 1275 (s), 1210 (w), 1170 (s), 1112 (w, br), 1053 (w), 1030 (sh), 974 (m), 898 (s), 880 (sh), 873 (s), 810 (s), 750 (m), 733 (m), 714 (s) cm^{-1} ; ¹H NMR 8.34 (2 H, s, *o*-H, lut), 6.89 (4 H, s, *m*-H, Mes), 6.39 (1 H, s, *p*-H, py), 2.34 (12 H, s, *o*-CH₃, Mes), 2.24 (6 H, s, *p*-CH₃, Mes), 1.47 (6 H, s, CH_3 , lut) -0.03 (3 H, s, AlCH_3); ¹³C NMR 154.3 (OC, Mes), 144.7 (*o*-C, lut), 142.2 (*p*-C, lut), 135.2 (*m*-C, lut), 129.4 (*m*-C, Mes), 126.5 (*p*-C, Mes), 126.3 (*o*-C, Mes), 20.7 (*p*-CH₃, Mes), 18.0 (*o*-CH₃, Mes), 17.5 (CH_3 , lut), -11.1 (AlCH_3). Anal. Calcd for $\text{C}_{26}\text{H}_{34}\text{AlNO}_2$: C, 74.44; H, 8.17; N, 3.34. Found: C, 74.00; H, 8.11; N, 3.40.

Al(OMes)₃(Py) (9a). To a pentane (40 mL) solution of MesOH (0.50 g, 3.67 mmol) was added AlMe_3 (0.61 mL, 1.22 mmol) via syringe. The resulting solution was stirred for 1 h and then py (0.5 mL, 6.2 mmol) was added. The resulting solution, which contained a large quantity of precipitate, was stirred an additional 8 h. After the precipitate settled, the pentane was removed via cannula and the remaining solid dried in vacuo. Crystals were grown from benzene/pentane: yield 0.53 g, 85%; mp 134–137 °C; IR 1635 (m), 1360 (sh), 1340 (s), 1305 (sh), 1290 (s), 1255

Table VII. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3 \text{ \AA}^2$) of the Non-Hydrogen Atoms in $\text{AlMe}(\text{OMes})_2(3,5\text{-Me}_2\text{py})$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Al(1)	7160 (3)	2020 (3)	5963 (1)	62 (1)
O(1)	7578 (5)	2271 (6)	4995 (3)	75 (3)
O(2)	8194 (5)	2620 (6)	6347 (3)	72 (3)
N(1)	7515 (7)	154 (7)	5835 (3)	59 (3)
C(1)	5500 (8)	2320 (10)	5630 (5)	88 (3)
C(2)	8555 (9)	-290 (9)	5777 (4)	67 (3)
C(3)	8874 (8)	-1578 (9)	5838 (4)	62 (3)
C(4)	8117 (7)	-2450 (9)	6002 (4)	59 (3)
C(5)	7044 (8)	-2022 (9)	6073 (4)	61 (3)
C(6)	6785 (8)	-724 (9)	5977 (4)	59 (3)
C(7)	10057 (8)	-2003 (10)	5752 (5)	96 (4)
C(8)	6202 (8)	-2967 (9)	6235 (5)	91 (3)
C(9)	7141 (8)	2719 (9)	4387 (5)	58 (3)
C(10)	6847 (8)	1834 (9)	3879 (4)	63 (3)
C(11)	6450 (7)	2324 (9)	3258 (4)	67 (3)
C(12)	6322 (8)	3629 (10)	3145 (4)	68 (3)
C(13)	6573 (7)	4488 (10)	3641 (4)	67 (3)
C(14)	6991 (7)	4048 (9)	4274 (4)	56 (3)
C(15)	6962 (9)	394 (9)	3999 (5)	95 (4)
C(16)	5871 (9)	4141 (11)	2460 (5)	103 (4)
C(17)	7284 (9)	4991 (9)	4824 (5)	91 (4)
C(18)	8782 (9)	3695 (10)	6631 (4)	63 (3)
C(19)	9826 (8)	4079 (9)	6501 (4)	67 (3)
C(20)	10435 (8)	5155 (9)	6823 (4)	70 (3)
C(21)	10024 (8)	5836 (10)	270 (4)	69 (3)
C(22)	8999 (8)	5429 (9)	7393 (4)	70 (3)
C(23)	8355 (8)	4380 (9)	7090 (4)	59 (3)
C(24)	10313 (9)	3360 (9)	6020 (5)	94 (4)
C(25)	10688 (9)	7017 (10)	7597 (5)	101 (4)
C(26)	7242 (8)	3975 (10)	7228 (4)	86 (3)

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

(w), 1195 (m), 1115 (m), 1060 (m), 1003 (m), 948 (sh), 932 (s), 898 (s), 844 (w), 808 (w), 780 (w), 763 (w), 747 (m) cm^{-1} ; ¹H NMR 8.53 (2 H, d, *J*(H-H) = 6.5 Hz, *o*-H, py), 6.83 (6 H, s, *m*-H, Mes), 6.60 (1 H, t, *J*(H-H) = 6.5 Hz, *p*-H, py), 6.23 (2 H, m, *m*-H, py), 2.27 (18 H, s, *o*-CH₃, Mes), 2.20 (9 H, s, *p*-CH₃, Mes); ¹³C NMR 153.4 (OC, Mes), 147.5 (*o*-C, py), 141.3 (*p*-C, py), 129.5 (*m*-C, Mes), 127.3 (*p*-C, Mes), 126.4 (*o*-C, Mes), 125.1 (*m*-C, py), 20.7 (*p*-CH₃, Mes), 17.8 (*o*-CH₃, Mes); ²⁷Al NMR 50 ($W_{1/2}$ = 3342 Hz). Anal. Calcd for C₃₂H₃₈AlNO₃: C, 75.12; H, 7.49; N, 2.74. Found: C, 75.30; H, 7.51; N, 2.74.

(MesO)₃Al(3,5-lutidine) (9b) was prepared in an analogous manner to 9a, with MesOH (0.25 g, 1.84 mmol), AlMe₃ (0.31 mL, 0.16 mmol), and 3,5-Me₂py (0.30 mL, 2.63 mmol): yield 0.26 g, 79%; mp 138–140 °C; IR 1735 (vw), 1615 (w), 1330 (s), 1290 (sh), 1282 (s), 1206 (w), 1190 (s), 1125 (w, br), 1075 (m), 1058 (m, br), 997 (m), 970 (w), 935 (s), 922 (s), 907 (sh), 893 (s), 848 (m), 778 (m), 762 (m), 740 (m) cm^{-1} ; ¹H NMR 8.42 (2 H, s, *o*-H, lut), 6.83 (6 H, s, *m*-H, Mes), 6.56 (1 H, s, *p*-H, lut), 2.34 (18 H, s, *o*-CH₃, Mes), 2.20 (9 H, s, *p*-CH₃, Mes), 1.65 (6 H, s, CH₃, lut); ¹³C 153.6 (OC, Mes), 146.6 (*o*-C, lut), 139.4 (*p*-C,

lut), 133.6 (*m*-C, lut), 129.4 (*m*-C, Mes), 127.1 (*p*-C, Mes), 126.5 (*o*-C, Mes), 20.7 (*p*-CH₃, Mes), 17.9 (*o*-CH₃, Mes), 17.7 (*m*-CH₃, lut); ²⁷Al NMR 50 ($W_{1/2}$ = 3400 Hz). Anal. Calcd for C₃₄H₄₂AlNO₃: C, 75.66; H, 7.84; N, 2.59. Found: C, 75.65; H, 7.81; N, 2.61.

X-ray Crystallographic Study. A crystal data summary is given in Table IV; fractional atomic coordinates are listed in Tables V–VII. X-ray data were collected on a Nicolet P3 (3a, 8b) diffractometer at room temperature and a Syntex P2₁ (7a) diffractometer, which is equipped with a modified LT-1 apparatus. Laue symmetry determination, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described techniques.¹⁴

All data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale by means of a Wilson plot. The systematic extinctions observed for all three determinations were *0k0* for *k* = 2*n* + 1 and *h0l* for *h* + *l* = 2*n* + 1; the diffraction symmetry was 2/*m*. The centrosymmetric monoclinic space group was *P*₂₁/*n*; a non-standard setting of *P*₂₁/*c* [*C*_{2h}; No 14] was uniquely defined.

All crystallographic calculations were carried out with either the UCI modified version of the UCLA Crystallographic Computing Package¹⁵ or the SHELXTL PLUS program set.¹⁶ The analytical scattering factors for neutral atoms were used through the analysis;¹⁷ both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion¹⁸ were included.

The structures were solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atom contributions were included by using a riding model with *d*(C-H) = 0.96 Å and *U*(iso) = 0.08 Å². Refinement of positional and anisotropic thermal parameters (isotropic for carbon atoms in 8b) led to convergence (see Table IV).

Acknowledgment. Financial support of this work is provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, ICI Wilton Materials Research Center, UK and ICI Americas, Wilmington, DE. Funds for the purchase of the Nicolet R3m/V diffractometer system were made available to UCI from the National Science Foundation under Grant CHE-85-14495. The assistance of Dr. A. Siedle, 3M Corporation, with the ²⁷Al NMR measurements is gratefully acknowledged.

Supplementary Material Available: Listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters (11 pages); tables of calculated and observed structure factors (28 pages). Ordering information is given on any current masthead page.

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