Synthesis and Reactivity of Bi-, Tri-, and Hexametallic and Zwitterionic Methyl Aluminum Complexes Containing a Phenoxide/Imine Ligand System

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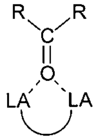
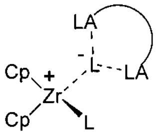
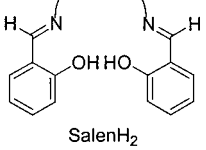
Addition of 3 equiv of trimethylaluminum to tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)methane, **1**H_3, affords the simple, C_3-symmetric, trimetallic species [**1**$(AlMe_2)_3$], **2**. To disrupt the Al_3O_3 bridging unit, one of the *ortho*-alkyl substituents from the tris(2-hydroxyphenyl)methane platform of **1**H_3 was substituted with a reactive aldehyde group to afford the ligands 3-(2,2′-methylenebis(4-methyl-6-*tert*-butylphenol)-5-methyl-2-hydroxybenzaldehyde, **3**H_3, and 3-(2,2′-methylenebis(4,6-di-*tert*-butylphenol)-5-methyl-2-hydroxybenzaldehyde, **4**H_3, respectively. Benzylamine reacts independently with both **3**H_3 and **4**H_3 specifically at the aldehyde functionality, affording the mixed donor ligands 3-(2,2′-methylenebis(4-methyl-6-*tert*-butylphenol)-5-methylsalicylidenebenzylimine, **5**H_3, and 3-(2,2′-methylenebis(4,6-di-*tert*-butylphenol)-5-methylsalicylidenebenzylimine, **6**H_3, in high isolable yields. Furthermore, the Salen-type ligand, **7**H_6, can be prepared from the reaction of 1,2-ethylenediamine and **4**H_3. Two equivalents of trimethylaluminum will react with **5**H_3 and **6**H_3 to produce the binuclear aluminum compounds [(**5**)Al_2Me_3], **8**, and [(**6**)Al_2Me_3], **9**, respectively. If an additional equivalent of trimethylaluminum is added to **9**, the trimetallic species [(**6**)Al_3Me_6], **10**, albeit as a slightly impure material, is observed, while **7**H_6 reacts in an analogous manner to afford [(**7**)Al_6Me_{12}], **11**. Treatment of **8** with 1 equiv of DMSO produces the new complex [(**5**)$\{AlMe_2\}$-$\{AlMe(OSMe_2)\}$], **12**, wherein the substrate is coordinated to only one of a possible two aluminum centers. In contrast to this simple transformation, the separate reactions of **8** and **9** with either cyclopentanone or cyclohexanone afford the zwitterionic mononuclear complexes [(**5**H)$^+$AlMe$^-$], **13**, and [(**6**H)$^+$AlMe$^-$], **14**. Solid-state structures are reported for **2**, **6**H_3, **7**H_6, and **9**−**13**.

Introduction

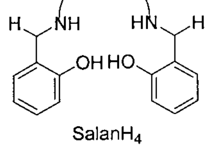
The preparation of Lewis acidic complexes with multiple metal centers has attracted much attention in recent years since complexes of this type could have utility in many important areas of chemistry including organic catalysis and anionic complexation.[1−3] If two Lewis acidic centers simultaneously bind a single Lewis base, the resulting complex should exhibit significantly enhanced reactivity relative to a similar monomeric species.[4] Given the Lewis acidity inherent in many group 13 complexes, cooperative binding of a substrate by these species offers the prospect for generation of extremely reactive compounds. Many new ligands have been designed solely for the task of placing two or more metals in proximity with the intention of binding Lewis bases.[1,5] With multiple donor groups, the mixed N_2O_2 and N_3O_2 donor ligands including the popular Salen[6]







SalenH$_2$



SalanH$_4$

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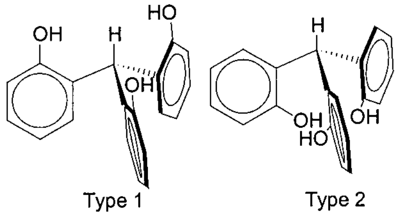
and Salan[7] derivatives would seem, at first glance, to be ideal framework for the preparation of multimetallic group 13 complexes, but the majority of work with this type of ligand has involved the preparation of monometallic group 13 complexes[8−12] for purposes such as selective addition of organic substrates.[13−15] In addition, these species include a number of interesting examples of cationic aluminum complexes[16−18] which may possess utility as polymerization cocatalysts. Apparently, the orientation and proximity of the four donor atoms in Salen-type ligands tend to favor the complexation of a single metal center in a square planar geometry. Monomeric group 13 complexes with high coordination numbers have been relatively popular, while,[19] until recently, relatively little attention has been devoted to multinuclear complexes,[20] specifically, binuclear moieties.[21] Contrary to initial studies,[22] more recent work has shown that binuclear complexes of mixed donor types N_xO_y are readily accessible and isolable.[21] Taking inspiration from the Salen platform and with the intent to prepare bimetallic group 13 complexes, we have developed a new class of ligand that contains one-half of the familiar phenol-imine donor set and a sterically encumbering, robust 2,2′-methylenebis(4-*tert*-butyl-6-alkylphenol) group. The two subunits of the ligand have been designed to each hold a single metal center, thus affording a novel binuclear aluminum species. Herein, we report the synthesis and characterization of aluminum complexes with these NO_3 donor ligands and the reactivity of the resulting complexes with Lewis bases.

Results and Discussion

Initial work in the development of simple multifunctional Lewis acid catalysts concentrated on a study of the reactivity of various Lewis acids with tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)methane, **1**H_3. This versatile, C_3-symmetric platform contains three phenolic donors all linked at the *ortho*-position to a central methine group. With three arms surrounding a central carbon, two distinct conformations can be envisaged for the ligand, type 1 and 2. In our extensive work with this class of ligand, a distinct preference for the type 1 conformer, with all three hydroxide groups aligned with the central methine hydrogen, has been noted.[23] The ligand can, however, be coaxed to adopt the type 2 conformer to bind atoms such as phosphorus and arsenic.[24] Nevertheless, when the ligand adopts the type 1 conformer, a single metal center cannot simultaneously bind all three phenolic arms since the atoms are separated by more than 4 Å and the methine hydrogen points directly between the donor groups. Consequently, deprotonation of **1**H_3 with akali metal[25] or zinc[26] reagents produces multimetallic clusters with the phenoxide donors bridging between adjacent metal sites. In these complexes, the metal sites are often buried within a hydrophobic pocket created by the *tert*-butyl substituents and the aryl rings. Due to their Lewis acidity, these species exhibit interesting properties including the ability to recognize molecules with a specific size and shape.[25] Unfortunately, despite their promise in the area of selective recognition, the complexes have thus far proven to be poor catalysts, and accordingly, we turned our attention to the reaction of **1**H_3 with significantly stronger Lewis acids such as aluminum, particularly in view of the spectacular utility of aluminum phenoxide complexes like methylaluminum 2,6-di-*tert*-butyl-4-methylphenolate (MAD).[27]



When a solution of trimethylaluminum is added to **1**H_3, the trimetallic species **2** is isolated in high yield as outlined in Scheme 1, and in sharp contrast to the diverse architectures produced when **1**H_3 is treated with dialkylzinc reagents,[26] the reaction with trimethylaluminum appears to form only the trimetallic species regardless of the stoichiometry and conditions. In **2**, each of the three phenoxides bridge between two $\{AlMe_2\}$ groups, forming a C_3-symmetric complex with

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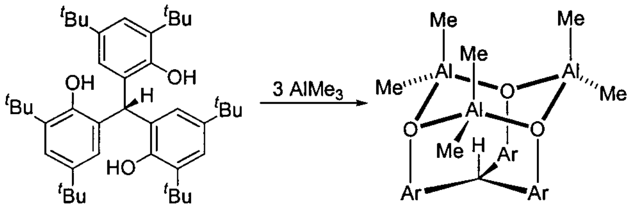
Table 1. X-ray Structural Data[a] for Compounds 2, 6H$_3$, 7H$_6$, and 9

	2	**6**H$_3$	**7**H$_6$·3THF	**9**·CH$_2$Cl$_2$·C$_5$H$_{12}$
total no. of reflns	17 529	22 551	9885	44 361
no. of unique reflns	11 891	7520	5893	6987
R(int)	0.0424	0.1082	0.0534	0.1192
θ_{max} (deg)	29.42	26.00	23.00	23.00
chemical formula	$C_{49}H_{79}Al_3O_3$	$C_{44}H_{57}NO_3$	$C_{88}H_{128}N_2O_9$	$C_{53}H_{77}NAl_2Cl_2O_3$
fw	797.06	647.91	1357.92	901.02
cryst syst	triclinic	monoclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	*Pbcn*
μ(Mo Kα) (mm^{-1})	0.112	0.069	0.067	0.206
a (Å)	11.4957(2)	11.5753(8)	10.1422(13)	28.448(2)
b (Å)	13.1039(2)	11.2030(7)	12.3607(16)	17.2688(13)
c (Å)	17.1580(2)	29.5529(19)	17.630(3)	20.4503(14)
α (deg)	75.540(1)	90.359(1)	84.566(6)	10046.4(12)
β (deg)	89.467(1)	3832.3(4)	75.120(5)	
γ (deg)	89.489(1)		88.961(6)	
V_c (Å^3)	2502.61(6)		2126.4(5)	
Z	2	4	1	8
R_1 [$I \geq 2\sigma(I)$ data][b]	0.0688 [6843]	0.0624 [3185]	0.0740 [2784]	0.0866 [4774]
wR_2 (all data)[c]	0.1719	0.1921	0.1912	0.2233
larg diff peak, hole (e/Å^3)	0.320,−0.355	0.276,−0.408	0.228,−0.226	0.577, −0.322

[a] Obtained with monochromatic Mo Kα radiation (λ = 0.71073 Å) at 173 K. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (XP)^2 + YP]$ where $P = (F_o^2 + 2F_c^2)/3\}$.

Scheme 1



1H$_3$ **2**

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2

Bond Lengths			
Al(1)−O(1)	1.903(2)	Al(2)−C(46)	1.947(3)
Al(1)−O(2)	1.895(2)	Al(2)−C(47)	1.945(3)
Al(1)−C(44)	1.947(3)	Al(3)−O(1)	1.918(2)
Al(1)−C(45)	1.943(3)	Al(3)−O(3)	1.908(2)
Al(2)−O(2)	1.897(2)	Al(3)−C(48)	1.948(3)
Al(2)−O(3)	1.906(2)	Al(3)−C(49)	1.948(3)
Al(1)···Al(2)	3.3747(12)	Al(2)···Al(3)	3.3576(12)
Al(1)···Al(3)	3.3726(12)		
Bond Angles			
O(1)−Al(1)−O(2)	100.92(8)	O(2)−Al(2)−C(47)	106.48(12)
O(1)−Al(1)−C(44)	107.21(12)	O(3)−Al(2)−C(46)	107.40(12)
O(2)−Al(1)−C(44)	108.83(12)	O(3)−Al(2)−C(47)	110.77(12)
O(1)−Al(1)−C(45)	110.84(12)	O(1)−Al(3)−O(3)	102.80(8)
O(2)−Al(1)−C(45)	106.40(12)	Al(1)−O(2)−Al(2)	125.70(10)
C(44)−Al(1)−C(45)	120.82(15)	Al(1)−O(1)−Al(3)	123.90(10)
O(2)−Al(2)−O(3)	100.84(8)	Al(2)−O(3)−Al(3)	123.36(10)
O(2)−Al(2)−C(46)	109.11(12)		

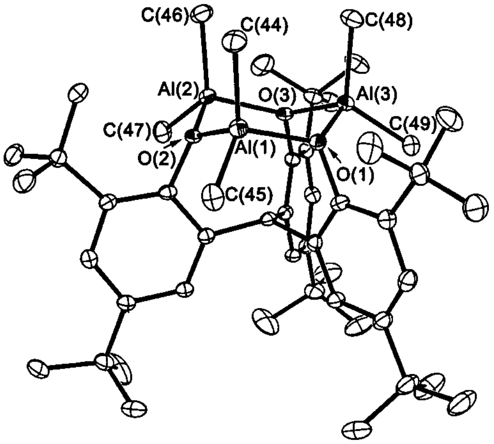


Figure 1. Diagram of the structure of **2** (30% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

an average Al−O distance of 1.905 Å (Table 2). In contrast to the familiar Al_2O_2 unit normally found when aluminum alkyls are bound by simple phenoxides or more complex ligands containing multiple phenoxide arms,[1,28,29] the methine hydrogen allows only the formation of an Al_3O_3 ring structure.[5b,30] As illustrated in Figure 1, the two alkyl groups bound to the metal center are in very different environments, and the shielding provided by the aryl rings is evident in the 1.52 ppm disparity in the two ^{1}H NMR resonances arising from the aluminum-methyl groups.

Since the aluminum centers in **2** are coordinately saturated and sterically congested by the *tert*-butyl substituents, the reactivity of the complex was not extensively investigated, but given the proximity of the metal centers, we reasoned the basic platform should allow for the preparation of reactive Lewis acid catalysts if the stabilizing Al_3O_3 ring structure is disrupted. The addition of a donor group at the periphery of the platform would effectively break the symmetry of the platform and preclude the formation of the Al_3O_3 unit, and efforts to derivatize **1**H$_3$ were undertaken. Several synthetic pathways have been used to prepare **1**H$_3$ including the acid-catalyzed condensation of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde with 2 equiv of 2,4-di-*tert*-butylphenol,[23a,24] and in an attempt to incorporate a reactive functionality at the periphery of the ligand,

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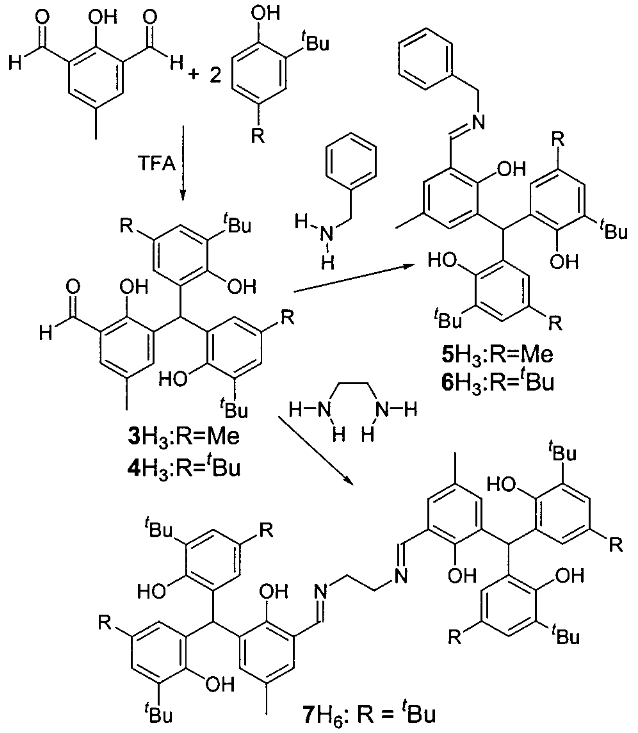
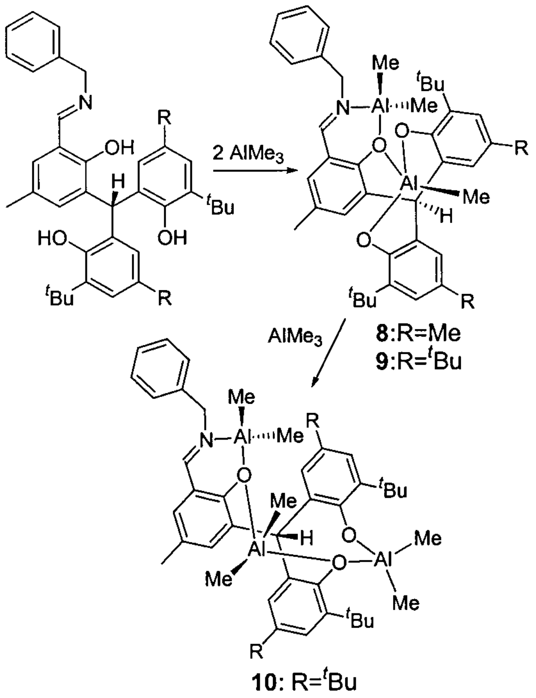
Scheme 2



2-hydroxy-5-alkyl-1,3-benzene dicarboxaldehydes were substituted for the normal salicylaldehyde precursor used to prepare **1**H_3. As outlined in Scheme 2, the reaction of the dialdehyde with 2,4-disubstituted phenols in trifluoroacetic acid will, under the proper conditions, afford 2-hydroxy-3-(2,2′-methylenebis(4-methyl-6-*tert*-butylphenol)-5-methylbenzaldehyde, **3**H_3, and 2-hydroxy-3-(2,2′-methylenebis(4,6-di-*tert*-butylphenol)-5-methylbenzaldehyde, **4**H_3, in which only one of the two aldehyde arms has reacted with the phenolic precursors. Although minor amounts of the product with four phenolic arms can be generated using a large excess of phenol, the insolubility of the product with one unreacted aldehyde arm in the reaction mixture allowed for its isolation in high yield and purity. Thus far, only ligands derived from 2,6-di-*tert*-butylphenol (**3**H_3) and 2-*tert*-butyl-4-methylphenol (**4**H_3) have been isolated and fully characterized, but the condensation reaction appears to be quite general.

With one aldehyde group tethered to the polyphenolic platform, mixed NO_3 donor ligands and even Salen-type complexes with N_2O_6 donors can easily be prepared with both **3**H_3 and **4**H_3 via nucleophilic attack by primary amines. Indeed, when **3**H_3 and **4**H_3 were reacted with benzylamine or ethylenediamine in ethanol, the Schiff base products **5**H_3, **6**H_3, and **7**H_6 were isolated in high yields as outlined in Scheme 2.[31] Much like **1**H_3, the three phenoxide donors in **5**H_3−**7**H_6 are aligned in a type 1 configuration in the solid state even with the imine groups bound to the framework as demonstrated in Figures 2 and 3. Interestingly, the ethylene backbone in **7**H_6 resides on an inversion symmetry position in the solid state with the two sets of phenoxide donors pointing in opposite directions. These groups are each, in turn, hydrogen-bonded to adjacent molecules, forming infinite polymeric chains of the ligand in the solid state.

Scheme 3



In view of the limited examples of mixed donor bimetallic aluminum complexes[21] and the potential of bimetallic Lewis acid catalysts,[1,2,4] the reactivity of **5**H_3, **6**H_3, and **7**H_6 with trimethylaluminum was examined. Initially, 2 equiv of trimethylaluminum was added to **5**H_3 and **6**H_3, independently (Scheme 3), and in both cases, comparable bimetallic products [(L)Al_2Me_3], **8** (L = **5**), and **9** (L = **6**), were isolated in high yield from pentane solutions. As can be seen in the diagram, the phenolic arms have adopted a type 2 orientation in order to bind both metal centers simultaneously. Moreover, with the formation of the type 2 geometry about the central methine carbon, a single metal, Al(1), coordinates all three oxygen donors and one methyl group in a tetrahedral arrangement. The imine arm in conjunction with one of the phenolic donors coordinates the second aluminum center, Al(2). The bridging phenoxide oxygen, O(3), is nearly equidistant between Al(1) and Al(2), with bond distances typical for phenoxide groups joining two aluminum centers[32,33] of 1.874(3) and 1.870(3) Å, respectively. For comparison, the two remaining Al(1)−O(1) bonds are more than a 0.1 Å shorter (Al(1)−O(1) = 1.742(3) and Al(1)−O(2) = 1.741(3) Å). Straddling the salicylidene phenolic oxygen and the imine donor, Al(2) fulfills its tetrahedral geometry with the incorporation of two methyl groups at an average distance of 1.940 Å similar to the metal sites observed in [Salcen(^{t}Bu){$AlMe_2$}$_2$] and [SalpenN_3H{$AlMe_2$}$_2$].[21f] In contrast to the values reported for the Salcen and Salpen species, the Al(2)−O(3) distance in **9** increases significantly to 1.870(3) Å due to the bridging interaction of O(3) with Al(1). There is, however, no significant change in the distance of the metal to the imine nitrogen in **9** relative to [Salcen(^{t}Bu){$AlMe_2$}$_2$] or [Sal(^{t}Bu)$AlEt_2$].[34]

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[31] Cottone, A.; Lecuivre, J. L.; Scott, M. J. Unpublished results.

[32] Applet, A. W.; Barron, A. R. *Organometallics* **1990**, *9*, 2137−2141.

[33] Haaland, A.; Stokkeland, O. *J. Organomet. Chem.* **1975**, *94*, 345−352.

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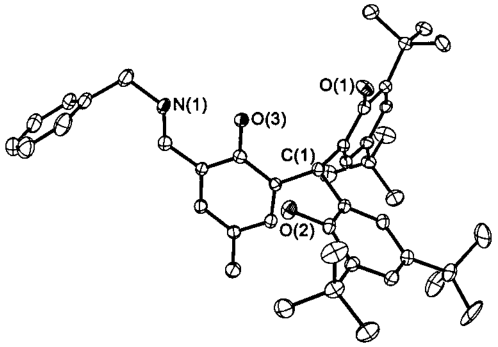

Figure 2. Diagram of the structure of **6**H_3 (30% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

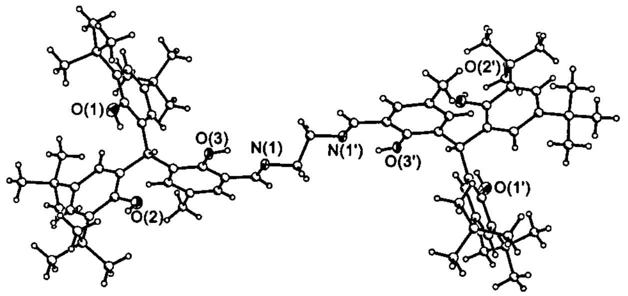

Figure 3. Diagram of the structure of **7**H_6 (30% probability ellipsoids). Primed and unprimed atoms are related by a center of inversion.

The ^{1}H NMR spectra of the crude reaction mixture after the addition of 2 equiv of trimethylaluminum to **5**H_3 and **6**H_3 consistently exhibited resonances arising from a very minor byproduct, which could be removed from the bimetallic products by recrystallization. If 3 equiv of trimethylaluminum were added to solutions of **5**H_3 and **6**H_3 or, alternatively, an additional equivalent of trimethylaluminum was added to solutions of **8** or **9**, the ratios of the signals arising from these byproducts increased markedly to the point where the bimetallic species was only a contaminant. The interpretation of the ^{1}H NMR spectra of the solutions was complicated due to the presence of two different products, but five distinct sets of resonances arising from Al-methyl groups could be identified. Unfortunately, every attempt to purify these materials was unsuccessful. Although single crystals of the complexes could be isolated, the product was consistently contaminated with small amounts of either **8** or **9**. The crystal structure of the product from the reaction of **9** and 1 equiv of trimethylaluminum was obtained, and the structure is presented in Figure 5 and Table 4. As depicted in Scheme 3, the product of the reaction is a trimetallic species [(**6**)Al_3Me_6], **10**, wherein the incoming aluminum center has caused Al(1) to lose one of the three phenoxide bonds found in **9**, allowing the arm to bind the incoming aluminum. The ligand has also inverted to adopt the type 1 orientation found in **6**H_3. Although **2** and **10** both contain three {$AlMe_2$} groups, the incorporation of the imine functionality has indeed disrupted the Al_3O_3 core as originally intended. The bond distances of the aluminum coordinated to the imine in **10** are indistinguishable from the analogous distances in **9**, but the remaining aluminum oxygen distances in **10** are all significantly longer than corresponding bonds in **9**, ranging from 1.757(2)° for Al(1)−O(1) to 1.931(3)° for Al(1)−O(2). Compounds **9** and **10** appear to be in equilibrium, and repeated recrystallization of solutions containing predominately **10** only increased the ratio of **9**.

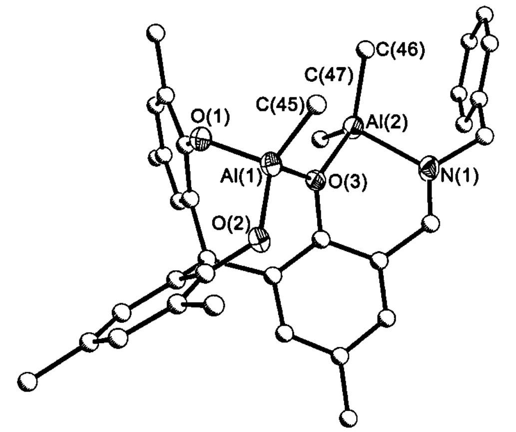

Figure 4. Diagram of the structure of **9** (30% probability ellipsoids; carbon atoms drawn with arbitrary radii). The *tert*-butyl methyl groups and all hydrogen atoms have been omitted for clarity.

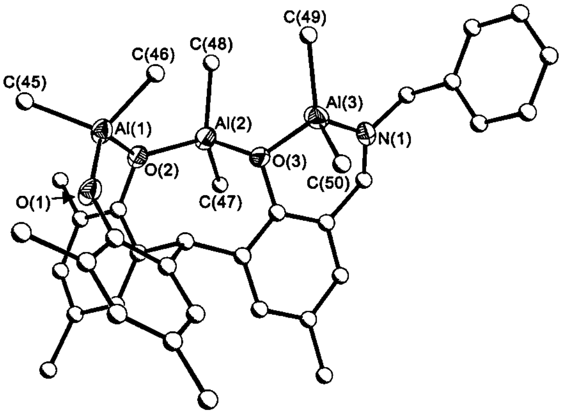

Figure 5. Diagram of the structure of **10** (30% probability ellipsoids; carbon atoms drawn with arbitrary radii). The *tert*-butyl methyl groups and all hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 9

	Bond Lengths		
Al(1)−O(1)	1.742(3)	Al(2)−O(3)	1.870(3)
Al(1)−O(2)	1.741(3)	Al(2)−C(46)	1.939(6)
Al(1)−O(3)	1.874(3)	Al(2)−C(47)	1.941(5)
Al(1)−C(45)	1.935(5)	Al(2)−N(1)	1.968(4)
Al(1)···Al(2)	3.3722(19)		
	Bond Angles		
O(1)−Al(1)−O(2)	107.59(15)	O(3)−Al(2)−C(46)	111.7(2)
O(1)−Al(1)−O(3)	102.65(14)	O(3)−Al(2)−C(47)	107.57(19)
O(2)−Al(1)−O(3)	103.08(14)	C(46)−Al(2)−C(47)	124.0(3)
O(1)−Al(1)−C(45)	116.3(2)	O(3)−Al(2)−N(1)	92.23(16)
O(2)−Al(1)−C(45)	113.74(19)	C(46)−Al(2)−N(1)	106.1(2)
O(3)−Al(1)−C(45)	112.15(19)	C(47)−Al(2)−N(1)	110.7(2)

In an attempt to obtain a clean sample of a product with this trimetallic unit, 6 equiv of trimethylaluminum was added to a solution of the Salen ligand **7**H_6 (Scheme 4). Earlier work had indicated that each imine/trisphenoxide half of this ligand reacts with

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(34) Hill, M. S.; Hutchison, A. R.; Keizer, T. S.; Parkin, S.; VanAelstyn, M. A.; Atwood, D. A. *J. Organomet. Chem.* **2001**, *628*, 71−75.

Table 4. X-ray Structural Data[a] for Compounds 10−13

	$\mathbf{10}\cdot C_5H_{12}$	$\mathbf{11}\cdot 2CHCl_3$	$\mathbf{12}\cdot 1^1/_4CH_2Cl_2$	$\mathbf{13}\cdot 2CH_2Cl_2$
total no. of reflns	23 758	23 326	32 324	20 355
no. of unique reflns	8481	7227	11 290	6093
R(int)	0.0746	0.1047	0.0893	0.1080
θ_{max} (deg)	23.50	23.00	28.34	23.50
chemical formula	$C_{55}H_{84}Al_3NO_3$	$C_{90}H_{136}N_2Al_6Cl_6O_6$	$C_{44.25}H_{59.5}NAl_2Cl_{2.5}O_4S$	$C_{41}H_{50}NAlCl_4O_3$
fw	888.17	1716.59	844.07	773.60
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
μ(Mo Kα) (mm^{-1})	0.112	0.262	0.292	0.346
a (Å)	11.3973(6)	13.3899(19)	12.7251(8)	9.5604(9)
b (Å)	22.8557(12)	21.173(3)	15.7782(10)	25.373(2)
c (Å)	22.6521(12)	18.885(3)	23.4282(14)	17.1538(16)
β (deg)	103.1290(10)	104.594(3)	99.951(1)	98.415(12)
V_c (Å^3)	5746.5(5)	5181.0(13)	4633.1(5)	4116.4(7)
Z	4	2	4	4
R_1 [$I \geq 2\sigma(I)$ data][b]	0.0729 [5753]	0.0889 [3854]	0.0549 [6103]	0.0705 [3066]
wR_2 (all data)[c]	0.1786	0.2194	0.1419	0.1522
larg diff peak, hole (e/Å^3)	0.246,−0.215	0.467,−0.412	0.418, −0.364	0.244, −0.222

[a] Obtained with monochromatic Mo Kα radiation (λ = 0.71073 Å) at 173 K. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (XP)^2 + YP]$ where $P = (F_o^2 + 2F_c^2)/3\}$.

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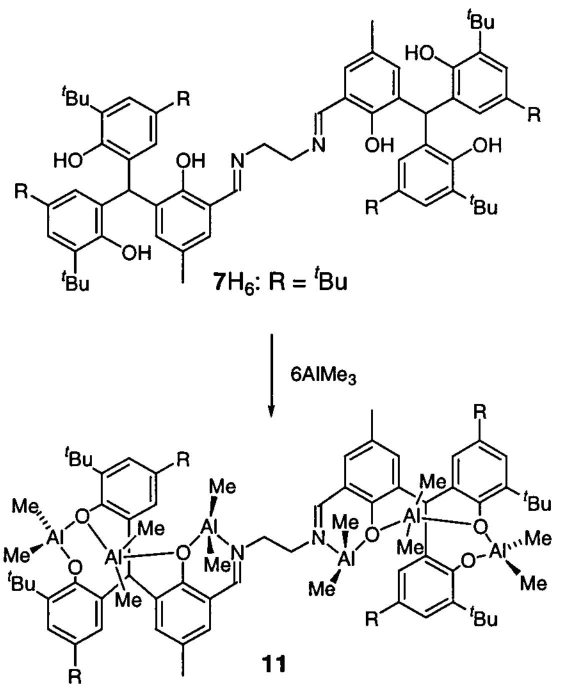
Scheme 4



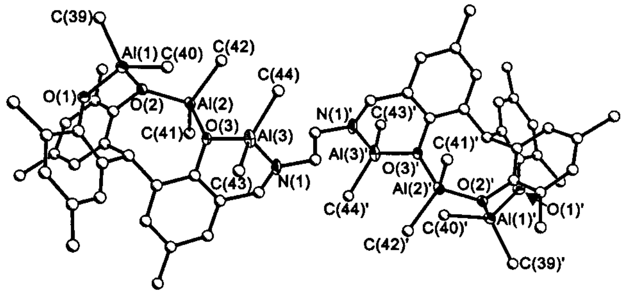


Figure 6. Diagram of the structure of **11** (30% probability ellipsoids; carbon atoms drawn with arbitrary radii). The *tert*-butyl methyl groups and all hydrogen atoms have been omitted for clarity. Primed and unprimed atoms are related by a center of inversion.

aluminum in a manner exactly analogous to both **5**H_3 and **6**H_3,[31] and indeed, the C_2 symmetric hexametallic species [(**7**)Al_6Me_{12}], **11**, consisting of two separate trimetallic species was isolated as shown in Figure 6. As highlighted in Table 5, the bond distances in **10** and **11** are identical and the data warrant no further discussion. Fortunately, the solubility properties of **11** allowed for a more detailed characterization of the compound relative to **10**, but presumably due to the presence of trace amounts of the bimetallic species [(**7**)-Al_4Me_6], crystalline **11** still failed to analyze satisfactorily.

With the intent to probe the interactions of Lewis bases with the binuclear aluminum complexes, the electron-rich DMSO compound was introduced into a solution of **8** (Scheme 5), and the clean conversion of **8** to a new species [(**5**){$AlMe_2$}{AlMe($OSMe_2$)}], **12**, was clearly evident in the ^{1}H NMR spectrum of the reaction mixture. Moreover, the spectrum exhibited only two resonances arising from methyl groups coordinated to an aluminum center, and these two peaks integrated in a ratio of 2:1. As illustrated in the solid-state structure of the complex depicted in Figure 7, the DMSO substrate disrupts the aryloxide bridge, Al(1)−O(3)−Al-(2), in **8** and coordinates to Al(1) in a η^1-O mode with a bond distance of 1.8238(16) Å. The geometry about this metal remains tetrahedral, with angles ranging between 100.36(7)° and 115.11(7)°, and there is a small but perceptible shortening of the bond between Al(1) and O(1) to 1.7169(16) Å. As expected, the disruption of the bridging interaction significantly shortens the distance from Al(2) to O(3) to 1.7726(15) Å, but in comparison to **8**, the remaining distances to Al(2) are not perturbed to any statistically significant extent. The inclusion of a coordinated DMSO molecule has induced the inversion of the phenolic arms with respect to the central methine carbon to a type 1 configuration with all three oxygen donors aligned with the methine hydrogen. The two metal centers are situated at a distance of 5.419(1) Å from each other.

In sharp contrast to reaction with DMSO, the addition of either cylcohexanone or cyclopentanone to **8** produced the same aluminum product, and the ^{1}H and ^{13}C NMR spectra of the material exhibited only a single resonance for a methyl group bound to aluminum. Moreover, the ^{1}H and ^{13}C NMR spectra indicated the isolated metal product did not contain the ketone substrate, and in the case of the reaction with cyclohexanone, the organic

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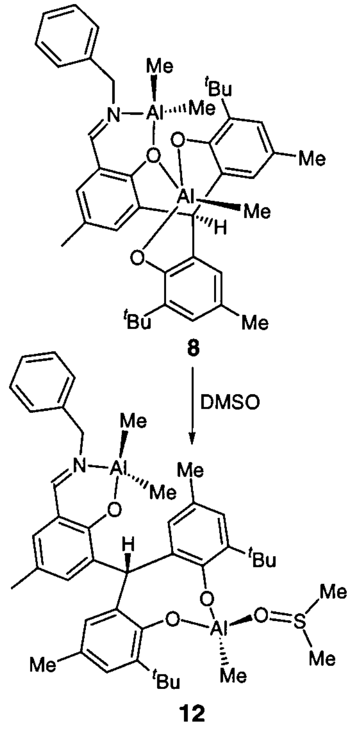
Table 5. Selected Bond Lengths (Å) and Angles (deg) for 10 and 11

10		**11**	
	Bond Lengths		
Al(1)−O(1)	1.757(2)	Al(1)−O(1)	1.768(4)
Al(1)−O(2)	1.931(3)	Al(1)−O(2)	1.957(4)
Al(1)−C(45)	1.952(4)	Al(1)−C(39)	1.961(6)
Al(1)−C(46)	1.947(4)	Al(1)−C(40)	1.956(6)
Al(2)−O(2)	1.859(2)	Al(2)−O(2)	1.842(4)
Al(2)−O(3)	1.914(3)	Al(2)−O(3)	1.930(4)
Al(2)−C(47)	1.954(4)	Al(2)−C(41)	1.954(6)
Al(2)−C(48)	1.948(4)	Al(2)−C(42)	1.946(6)
Al(3)−O(3)	1.879(3)	Al(3)−O(3)	1.858(4)
Al(3)−C(49)	1.937(4)	Al(3)−C(43)	1.911(7)
Al(3)−C(50)	1.935(4)	Al(3)−C(44)	1.953(7)
Al(3)−N(1)	1.976(3)	Al(3)−N(1)	1.980(6)
Al(1)···Al(2)	3.4015(15)	Al(1)···Al(2)	3.420(2)
Al(2)···Al(3)	3.5043(18)	Al(2)···Al(3)	3.441(3)
	Bond Angles		
10		**11**	
O(1)−Al(1)−O(2)	109.40(12)	O(1)−Al(1)−O(2)	106.88(18)
O(1)−Al(1)−C(45)	107.03(14)	O(1)−Al(1)−C(39)	108.9(2)
O(1)−Al(1)−C(46)	112.20(15)	O(1)−Al(1)−C(40)	111.0(3)
O(2)−Al(1)−C(45)	107.68(15)	O(2)−Al(1)−C(39)	106.6(2)
O(2)−Al(1)−C(46)	106.14(15)	O(2)−Al(1)−C(40)	104.1(2)
C(45)−Al(1)−C(46)	114.26(19)	C(39)−Al(1)−C(40)	118.6(3)
O(2)−Al(2)−O(3)	104.60(11)	O(2)−Al(2)−O(3)	107.07(17)
O(2)−Al(2)−C(47)	108.78(16)	O(2)−Al(2)−C(41)	110.6(2)
O(2)−Al(2)−C(48)	112.29(15)	O(2)−Al(2)−C(42)	108.2(2)
O(3)−Al(2)−C(47)	104.55(14)	O(3)−Al(2)−C(41)	101.2(2)
O(3)−Al(2)−C(48)	107.65(17)	O(3)−Al(2)−C(42)	109.5(2)
C(47)−Al(2)−C(48)	117.85(19)	C(41)−Al(2)−C(42)	119.6(3)
O(3)−Al(3)−C(49)	117.82(18)	O(3)−Al(3)−C(43)	106.9(3)
O(3)−Al(3)−C(50)	107.09(15)	O(3)−Al(3)−C(44)	119.2(3)
C(49)−Al(3)−C(50)	121.4(2)	C(43)−Al(3)−C(44)	119.8(3)
O(3)−Al(3)−N(1)	88.91(12)	O(3)−Al(3)−N(1)	89.5(2)
C(49)−Al(3)−N(1)	107.84(17)	C(43)−Al(3)−N(1)	110.5(3)
C(50)−Al(3)−N(1)	108.71(16)	C(44)−Al(3)−N(1)	106.6(3)
Al(1)−O(2)−Al(2)	127.62(15)	Al(1)−O(2)−Al(2)	128.3(2)
Al(2)−O(3)−Al(3)	135.04(13)	Al(2)−O(3)−Al(3)	130.6(2)

Scheme 5



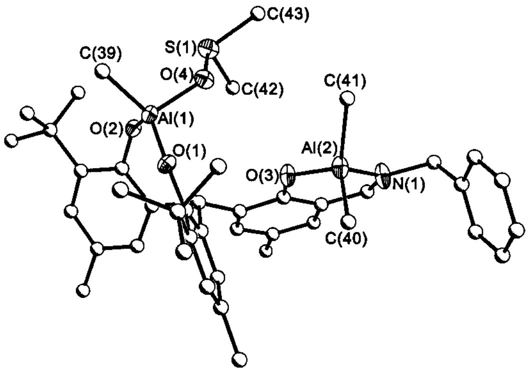


Figure 7. Diagram of the structure of **12** (30% probability ellipsoids; carbon atoms drawn with arbitrary radii). Hydrogen atoms have been omitted for clarity.

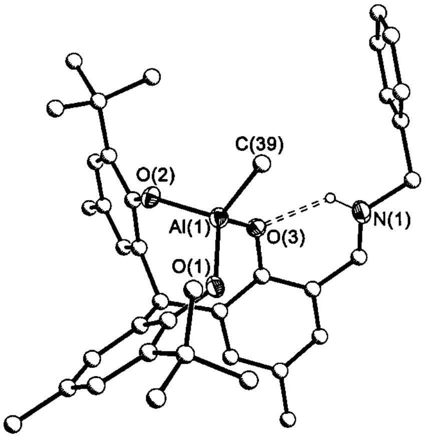


Figure 8. Diagram of the structure of **13** (30% probability ellipsoids; carbon atoms drawn with arbitrary radii). Hydrogen atoms have been omitted for clarity.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 12

	Bond Lengths		
Al(1)−O(1)	1.7169(16)	Al(2)−O(3)	1.7726(15)
Al(1)−O(2)	1.7553(15)	Al(2)−C(40)	1.943(3)
Al(1)−O(4)	1.8238(16)	Al(2)−C(41)	1.961(3)
Al(1)−C(39)	1.949(2)	Al(2)−N(1)	1.980(2)
Al(1)···Al(2)	5.4191(9)		
	Bond Angles		
O(1)−Al(1)−O(2)	115.11(7)	O(3)−Al(2)−C(40)	110.39(10)
O(1)−Al(1)−O(4)	107.31(7)	O(3)−Al(2)−C(41)	110.37(10)
O(2)−Al(1)−O(4)	100.36(7)	C(40)−Al(2)−C(41)	122.84(13)
O(1)−Al(1)−C(39)	111.10(10)	O(3)−Al(2)−N(1)	93.66(8)
O(2)−Al(1)−C(39)	114.43(9)	C(40)−Al(2)−N(1)	110.19(11)
O(4)−Al(1)−C(39)	107.42(11)	C(41)−Al(2)−N(1)	105.32(11)
Al(1)−O(4)−S(1)	123.01(9)		

Table 7. Selected Bond Lengths (Å) and Angles (deg) for 13

	Bond Lengths		
Al(1)−O(1)	1.742(3)	Al(1)−O(3)	1.797(3)
Al(1)−O(2)	1.751(3)	Al(1)−C(39)	1.944(4)
	Bond Angles		
O(1)−Al(1)−O(2)	108.04(16)	O(1)−Al(1)−C(39)	113.50(19)
O(1)−Al(1)−O(3)	102.80(15)	O(2)−Al(1)−C(39)	115.5(2)
O(2)−Al(1)−O(3)	107.43(15)	O(3)−Al(1)−C(39)	108.68(19)

product bicyclohexyliden-2-one was isolated and characterized from the reaction mixture. As illustrated in the solid-state structure of **13** (Figure 8; Table 7) and in Scheme 6, the reaction with cyclohexanone produced a mononuclear zwitterionic aluminum complex, [(**5**H)$^+$-AlMe$^-$], **13**, in addition to the aldol condensation product bicyclohexyliden-2-one, which was isolated and characterized. Similar aldol condensation chemistry has been seen with $Cl_2AlCH_2TiCl_3$,[35] and no attempt was made to ascertain the fate of the $AlMe_2$ unit lost from **8** during

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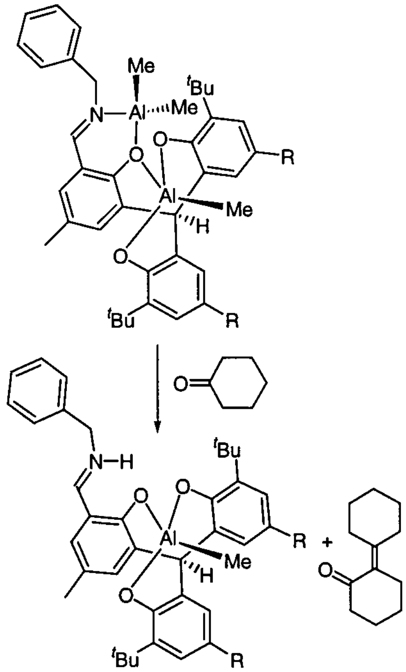
Scheme 6



13:R=Me
14:R=^{t}Bu

the course of the reaction. Compound **9** reacted with cyclohexanone in an analogous manner to afford $[(\mathbf{6}H)^+AlMe^-]$, **14**.

Unlike the transformation from **8** to **12**, the conversion of **8** to **13** conserves the geometry about the central methine carbon. Once again, the angles around the aluminum center are unspectacular and range from 102.81(15)° to 115.5(2)°. The Al(1)−O(1) and Al(1)−O(2) distances are 1.742(3) and 1.751(3) Å, respectively, and are shorter than the corresponding Al(1)−O(3) bond distance of 1.797(3) Å. We attribute this slight elongation of the Al(1)−O(3) bond to the formation of a hydrogen bond to the protonated imine and not protonation of the oxygen atom. During the refinement of the X-ray crystal structure, the largest peak in the final difference Fourier map was located ~1.0 Å from the imine nitrogen atom, and this position isotropically refined to a distance of 0.92(6) and 1.88(6) Å from N(1) and O(1), respectively. Further suggesting the formation of zwitterions in **13** and **14**, Barron and co-workers have identified a preference for a zwitterionic alkoxide/ammonium species rather than the alcohol/amine complex in the case of the reaction of $HOCH_2CH_2CH_2NMe_2$ with $Al(^tBu)_3$.[36]

Conclusions

The reaction of trimethylaluminum with the ligand tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)methane affords a C_3-symmetric trimetallic complex wherein the metals are coordinatively saturated and sterically congested. With the intention of disrupting the formation of a stabilizing Al_3O_3 unit found in this species, several mixed donor ligands of the type NO_3 have been synthesized and used to prepare a new class of bifunctional aluminum species **8** and **9** containing a stabilizing phenoxide bridge between the two metal centers. Despite the presence of the bridge, the complexes are susceptible to further reactivity, as evidenced by the formation of the unusual trimetallic species **10** upon the addition of 1 equiv of aluminum to solutions of **9**. Moreover, Lewis bases such as DMSO will induce the cleavage of one of the aluminum oxygen bonds involved in the bridging interaction in the bimetallic species, allowing for the isolation of new bimetallic species containing a coordinated Lewis base in proximity to the second aluminum center. Both **8** and **9** will also react with the Lewis bases cyclopentanone and cyclohexanone to afford a monometallic, zwitterionic product as well as the organic aldol condensation product. Work has now begun on a study of the ability of the bimetallic complexes **8** and **9** to catalyze organic transformations, and efforts to adjust the constraints of the ligand system to enhance cooperativity in these reactions are also underway.

Experimental Section

Unless otherwise stated, all manipulations were carried out under an inert atmosphere of N_2 in a drybox or on a vacuum line using standard Schlenk techniques. All solvents used were dried and distilled prior to use. All NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer at 299.95 and 75.47 MHz for the proton and carbon channels, respectively, or on a Varian VXR 300 MHz spectrometer at 78.17 MHz for the aluminum channel. Chemicals shifts (δ) are reported with reference to $[Al(H_2O)_6]Cl_3$ for ^{27}Al spectra. IR spectra were recorded as KBr pellets on a Bruker Vector instrument at a resolution of 2 cm^{-1}. Elemental analyses were performed at Atlantic Microlab Inc., Norcross, GA, or Complete Analysis Laboratories Inc., Parsippany, NJ. Tris(3,5-di-*tert*-buyl-2-hydroxyphenyl)methane[23] and 2-hydroxy-5-methyl-1,3-benzene dicarboxaldehyde[37] were prepared as previously described.

Synthesis of [(Tris(3,5-di-*tert*-butyl-2-phenoxy)methane)Al_3Me_6], 2. A 2.0 M solution of trimethylaluminum in toluene (2.38 mmol, 1.19 mL) was added to a cooled (0 °C) solution of 0.50 g (0.79 mmol) of tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)methane in 20 mL of toluene. The mixture was slowly allowed to warm to room temperature, and the solution was stirred overnight. The solvent was removed in vacuo, and the residue was redissolved in a minimal amount of pentane and filtered. The filtrate was stored at −30 °C, and the resultant crystalline material was collected by filtration and dried to yield 0.50 g of product. Yield: 78%. Anal. Calcd for $C_{49}H_{79}Al_3O_3$: C, 73.83; H, 9.99. Found: C, 74.12; H, 10.16. ^1H NMR (CD_2Cl_2): δ 8.42 (s, 1H, C*H*), 7.81 (d, $J = 2.44$ Hz, 3H, aryl-*H*), 7.27 (d, $J = 2.44$ Hz, 3H, aryl-*H*), 1.39 (s, 27H, ^{t}Bu), 1.32 (s, 27H, ^{t}Bu), −0.18 (s, 9H, Al-CH_3), −1.70 (s, 9H, Al-CH_3). ^{13}C NMR (CD_2Cl_2): δ 150.9 (aryl), 148.3 (aryl), 139.1 (aryl), 136.1 (aryl), 124.9 (aryl), 123.7 (aryl), 36.3 (^{t}Bu), 35.0 (^{t}Bu), 32.6 (^{t}Bu), 31.7 (^{t}Bu), 27.9 (CH), −6.2 (Al-Me), −8.7 (Al-Me). ^{27}Al NMR (CD_2Cl_2): δ 63 $\omega_{1/2}$ 3.9 kHz.

Synthesis of 3-(2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol)-5-methyl-2-hydroxybenzaldehyde, $3H_3$. A 2.20 g (13.4 mmol) portion of 2-hydroxy-5-methyl-1,3-benzene dicarboxaldehyde was added to 2-*tert*-butyl-4-methylphenol (5.50 g, 33.5 mmol). Trifluoroacetic acid (10 mL) was added in 1 mL aliquots over a period of several minutes, and the mixture was stirred for 3 h. The resultant pink precipitate was isolated and washed with cold methanol and dried in vacuo to yield 4.53 g

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(72%) of product as an off-white powder. Anal. Calcd for $C_{31}H_{38}O_4$: C, 78.44; H, 8.07. Found: C, 77.97; H, 8.35. IR (KBr, ν_{max}/cm^{-1}): 3462m, 3299m, 3000m, 2954s, 2866m, 1634s, 1443s, 1389m, 1306m, 1254s, 1234s, 1213s, 1163s, 1003s, 884m, 764m, 711m, 669m, 502m. ^{1}H NMR ($CDCl_3$): δ 11.32 (br s, O*H*, 1H), 9.88 (s, *H*C═O, 1H), 7.32 (d, aryl-*H*, J = 2.1 Hz, 1H), 7.06 (d, aryl-*H*, J = 1.9 Hz, 1H), 7.05 (d, aryl-*H*, J = 1.9 Hz, 2H), 6.53 (d, aryl-*H*, J = 1.7 Hz, 2H), 5.92 (s, C*H*, 1H), 4.94 (br s, O*H*, 2H), 2.28 (s, Me, 3H), 2.19 (s, Me, 6H), 1.35 (s, *tert*-Bu, 18H). ^{13}C NMR: δ 196.8 (H*C*═O), 156.9 (aryl), 151.2 (aryl), 138.8 (aryl), 137.8 (aryl), 133.0 (aryl), 129.7 (aryl), 129.6 (aryl), 129.3 (aryl), 127.6 (aryl), 127.5 (aryl), 127.0 (aryl), 120.5 (aryl), 39.3 (*C*H), 34.9 (^{t}Bu), 30.0 (^{t}Bu), 21.3 (Me), 20.8 (Me). High-resolution FAB-MS: calcd 474.277 (M$^+$), found 474.276.

Synthesis of 3-(2,2′-Methylenebis(4,6-di-*tert*-butylphenol)-5-methyl-2-hydroxybenzaldehyde, 4H$_3$. A 2.20 g (13.4 mmol) portion of 2-hydroxy-5-methyl-1,3-benzene dicarboxaldehyde was added to 2,4-di-*tert*-butylphenol (6.90 g, 33.5 mmol), and the reaction mixture was treated in a manner similar to **1**H$_3$ to yield 5.75 g (77%) of product as a pink solid. Crystals suitable for elemental analysis were obtained from an evaporation of a saturated acetone solution. Anal. Calcd for $C_{37}H_{50}O_4 \cdot C_3H_6O$: C, 77.87; H, 9.16. Found: C, 77.97; H, 9.50. IR (KBr, ν_{max}/cm^{-1}): 3627w, 3528m, 2964s, 2904s, 2871s, 1659s, 1619m, 1599m, 1459s, 1360s, 1310s, 1264s, 1181s, 885m, 768m, 668m, 476w. ^{1}H NMR ($CDCl_3$): δ 11.39 (s, O*H*, 1H). 9.83 (s, *H*C═O, 1H), 7.31 (s, aryl-*H*, 1H), 7.27 (d, aryl-*H*, J = 2.0 Hz, 1H), 7.02 (s, aryl-*H*, 1H), 6.69 (d, aryl-*H*, J = 1.8 Hz, 2H), 6.07 (s, C*H*, 1H), 3.95 (br s, O*H*, 2H), 2.26 (s, Me, 3H), 1.39 (s, ^{t}Bu, 18H), 1.17 (s, *tert*-Bu, 18H). ^{13}C NMR: δ 197.1 (H*C*═O), 156.8 (aryl), 150.6 (aryl), 142.5 (aryl), 138.5 (aryl), 137.1 (aryl), 132.7 (aryl), 130.4 (aryl), 129.3 (aryl), 127.4 (aryl), 124.0 (aryl), 122.9 (aryl), 120.2 (aryl), 38.3 (*C*H), 35.0 (^{t}Bu), 34.3 (^{t}Bu), 31.5 (^{t}Bu), 29.6 (^{t}Bu), 20.5 (Me). High-resolution FAB-MS: calcd 558.371 (M$^+$), found 558.370.

Synthesis of 3-(2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol)-5-methylsalicylidenebenzylimine, 5H$_3$. A portion of **3**H$_3$ (2.61 g, 5.50 mmol) was dissolved in ethanol (100 mL) with benzylamine (0.60 mL, 5.54 mmol). The reaction was refluxed for 12 h, resulting in the formation of a yellow precipitate. The solid was collected and dried in vacuo overnight to afford 2.85 g of product (92%). Anal. Calcd for $C_{38}H_{45}NO_3$: C, 80.95; H, 8.05; N, 2.49. Found: C, 80.94; H, 8.46; N, 2.15. IR (KBr, ν_{max}/cm^{-1}): 3497s, 3127m (O−H stretch), 2950s, 2917m, 2871m, 1636s (C═N stretch), 1443s, 1400s, 1362m, 1247m, 1181m, 866w, 767w, 699w. ^{1}H NMR ($CDCl_3$): δ 14.22 (s, O*H*, 1H), 8.31 (s, *H*C═N, 1H), 7.25−7.36 (m, benzyl-*H*, 5H), 7.02 (d, aryl-*H*, J = 1.9 Hz, 2H), 6.98 (d, aryl-*H*, J = 1.9 Hz, 2H), 6.65 (d, aryl-*H*, J = 1.9 Hz, 2H), 5.94 (s, C*H*, 1H), 5.42 (br s, O*H*, 2H), 4.75 (s, *H*$_2$C-N, 2H), 2.21 (s, Me, 3H), 2.18 (s, Me, 6H), 1.35 (s, ^{t}Bu, 18H). ^{13}C NMR: δ 165.5 (N═*C*H), 158.0 (aryl), 151.2 (aryl), 137.7 (aryl), 137.6 (aryl), 134.5 (aryl), 131.0 (aryl), 129.1 (aryl), 128.9 (aryl), 128.7 (aryl), 128.1 (aryl), 127.8 (aryl), 127.7 (aryl), 127.6 (aryl), 127.5 (aryl), 127.1 (aryl), 118.2 (aryl), 62.3 (N-*C*H$_2$), 39.2 (*C*H), 34.9 (^{t}Bu), 29.9 (^{t}Bu), 21.3 (Me), 20.8 (Me). High-resolution FAB-MS: calcd 563.340 (M$^+$), found 563.341.

Synthesis of 3-(2,2′-Methylenebis(4,6-di-*tert*-butylphenol)-5-methylsalicylidenebenzylimine, 6H$_3$. A portion of **4**H$_3$ (2.40 g, 4.30 mmol) was dissolved in ethanol (100 mL) with benzylamine (0.47 mL, 4.30 mmol). The reaction was heated under reflux overnight, resulting in the formation of a precipitate. The yellow solid was collected by filtration and dried in vacuo to afford 2.31 g of product (83%). Anal. Calcd for $C_{44}H_{57}NO_3$: C, 81.56; H, 8.87; N, 2.16. Found: C, 81.34; H, 9.25; N, 2.15. IR (KBr, ν_{max}/cm^{-1}): 3386m (O−H stretch), 2950s, 2865m, 1636s (C═N stretch), 1535m, 1477s, 1360s, 1294m, 1198s, 1149m, 880w, 757w, 702m, 661w. ^{1}H NMR ($CDCl_3$): δ 14.36 (s, O*H*, 1H), 8.33 (s, *H*C═N, 1H), 7.25−7.37 (m, benzyl-*H*, 5H), 7.23 (d, aryl-*H*, J = 2.1 Hz, 2H), 7.00 (d, aryl-*H*, J = 3.9 Hz, 2H), 6.88 (d, aryl-*H*, J = 2.3 Hz, 2H), 6.02 (s, C*H*, 1H), 5.58 (s, O*H*, 2H), 4.77 (s, N-C*H*$_2$, 2H), 2.22 (s, Me, 3H), 1.37 (s, Me, 6H), 1.19 (s, ^{t}Bu, 18H). ^{13}C NMR: δ 165.6 (N═*C*H), 158.0 (aryl), 151.1 (aryl), 142.1 (aryl), 137.7 (aryl), 136.9 (aryl), 134.5 (aryl), 130.9 (aryl), 129.2 (aryl), 129.0 (aryl), 128.1 (aryl), 127.9 (aryl), 127.8 (aryl), 127.1 (aryl), 124.2 (aryl), 123.0 (aryl), 118.2 (aryl), 62.3 (N-*C*H$_2$), 38.7 (*C*H), 35.2 (^{t}Bu), 34.5 (^{t}Bu), 31.8 (^{t}Bu), 30.1 (*t*Bu), 20.8 (Me).

Synthesis of *N,N*′-Bis{3-[2,2′-methylenebis(4,6-di-*tert*-butylphenol)-5-methylsalicylidene]}-1,2-ethylenediamine, 7H$_6$. A 1.00 g portion of **4**H$_3$ (1.79 mmol) was dissolved in 40 mL of ethanol, and 59 μL (0.89 mmol) of 1,2-ethylenediamine was added. The mixture was refluxed for 12 h and cooled to room temperature, and the yellow microcrystalline solid was collected by filtration. The product was washed with cold methanol (4 × 10 mL) and dried under vacuum to yield 0.85 g of solid. Yield: 83%. Anal. Calcd for $C_{76}H_{104}N_2O_6$: C, 79.96; H, 9.18; N, 2.45. Found: C, 80.13; H, 9.23; N, 2.34. IR (KBr, ν_{max}/cm^{-1}): 3562m, 3522m, 3451w, 2952s, 2910m, 2871m, 1636s (C═N stretch), 1599w, 1470s, 1443m, 1319m, 1363m, 1290m, 1268m, 1189s, 1029w, 980w, 888w, 770w, 658w, 569w, 471w. ^{1}H NMR ($CDCl_3$): δ 14.07 (s, br, 2H, O*H*), 8.25 (s, 2H, N═C*H*), 7.23 (d, J = 1.95 Hz, 4H, Ar-*H*), 6.97 (s, 2H, Ar-*H*), 6.93 (s, 2H, Ar-*H*), 6.85 (d, J = 1.95 Hz, 4H, Ar-*H*), 6.00 (s, 2H, C*H*), 5.51 (s, 4H, O*H*), 3.91 (s, 4H, N-C*H*$_2$), 2.16 (s, 6H, C*H*$_3$), 1.37 (s, 36H, ^{t}Bu), 1.17 (s, 36H, ^{t}Bu). ^{13}C NMR ($CDCl_3$): δ 166.9 (N═*C*H), 157.1 (aryl), 151.0 (aryl), 142.1 (aryl), 136.8 (aryl), 134.5 (aryl), 131.1 (aryl), 128.6 (aryl), 128.1 (aryl), 127.0 (aryl), 124.1 (aryl), 122.9 (aryl), 118.0 (aryl), 59.0 (N-*C*H$_2$), 38.4 (*C*H), 35.2 (^{t}Bu), 34.5 (^{t}Bu), 31.7 (^{t}Bu), 30.0 (^{t}Bu), 20.7 (Me). A crystal suitable for an X-ray determination was obtained by slow evaporation of a solution of **7** in THF.

Preparation of [(5)Al$_2$Me$_3$], 8. A 2.0 M solution of trimethylaluminum in toluene (0.95 mL, 1.90 mmol) was added to a solution of **5**H$_3$ (0.53 g, 0.95 mmol) in toluene (50 mL) at 0 °C. The reaction was held at 0 °C for 1 h and was gradually allowed to warm to room temperature. After 4 h, the solvent was removed, and the residue was dissolved in pentane (25 mL) and stirred at ambient conditions for an additional hour. A precipitate formed and was isolated and dried to yield 0.39 g of a yellow powder (63%). Crystals suitable for X-ray and elemental analysis were obtained from a saturated methylene chloride solution. Anal. Calcd for $C_{41}H_{51}NAl_2O_3$: C, 74.63; H, 7.79; N, 2.12. Found: C, 74.52; H, 7.79; N, 2.09. IR (KBr, ν_{max}/cm^{-1}): 3438w, 3151w, 2958s, 2923m, 2858m, 1624s (C═N stretch), 1583m, 1554w, 1470s, 1444s, 1397m, 1352w, 1293m, 1270m, 1208m, 1163w, 1065w, 1026w, 895w, 863s, 801s, 758m, 752m, 698s, 674s, 556w, 497w, 445w. ^{1}H NMR ($CDCl_3$): δ 8.17 (s, N═C*H*, 1H), 7.37 (d, aryl-*H*, J = 1.8 Hz, 1H), 7.16−7.34 (m, benzyl-*H*, 6H), 6.96 (d, aryl-*H*, J = 1.7 Hz, 1H), 6.90 (br s, aryl-*H*, 2H), 6.82 (br s, aryl-*H*, 1H), 6.75 (br s, aryl-*H*, 1H), 5.16 (s, C*H*, 1H), 4.67−4.85 (m, N-C*H*$_2$, 2H), 2.23 (s, Me, 3H), 2.14 (s, Me, 3H), 1.29 (s, ^{t}Bu, 18H), −0.59 (s, Al-C*H*$_3$, 3H), −0.68 (s, Al-C*H*$_3$, 3H), −1.91 (s, Al-C*H*$_3$, 3H). ^{13}C NMR: δ 170.5 (N═*C*H), 156.4 (aryl), 155.9 (aryl), 149.9 (aryl), 140.9 (aryl), 139.5 (aryl), 139.2 (aryl), 138.9 (aryl), 133.9 (aryl), 133.1 (aryl), 132.5 (aryl), 131.3 (aryl), 130.2 (aryl), 129.7 (aryl), 129.5 (aryl), 129.4 (aryl), 129.0 (aryl), 126.9 (aryl), 126.4 (aryl), 125.7 (aryl), 125.6 (aryl), 121.7 (aryl), 61.7 (N-*C*H$_2$), 57.6 (*C*H), 35.2 (^{t}Bu), 34.8 (^{t}Bu), 30.7 (^{t}Bu), 30.3 (^{t}Bu), 20.9 (Me), 20.8 (Me), 20.4 (Me), −10.0 (Al-Me), −11.8 (Al-Me), −13.9 (Al-Me). ^{27}Al NMR ($CDCl_3$): δ 61 $\omega_{1/2}$ 5.8 kHz. High-resolution FAB-MS: calcd 659.350 (M$^+$), found 659.350.

Preparation of [(6)Al$_2$Me$_3$], 9. A 2.0 M solution of trimethylaluminum in toluene (0.77 mL, 1.54 mmol) was added to a solution of **6**H$_3$ (0.50 g, 0.772 mmol) in toluene (50 mL) at 0 °C. The sealed reaction vessel was immersed in an ice−water bath for 1 h and slowly allowed to warm to room temperature. The solvent was removed under vacuum after 4 h, and the residue was redissolved in pentane (25 mL) and stirred at ambient conditions for an additional hour. A precipitate formed and was isolated, washed with cold pentane, and dried to yield

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0.50 g of product as a yellow powder (77%). Crystals suitable for elemental analysis were obtained from a saturated chloroform solution. Anal. Calcd for $C_{47}H_{63}NAl_2O_3$: C, 75.88; H, 8.54; N, 1.88. Found: C, 75.82; H, 8.59; N, 1.80. IR (KBr, ν_{max}/cm^{-1}): 3425w, 3158w, 2956s, 2904m, 2865s, 1628m (C═N stretch), 1580w, 1554w, 1476s, 1444s, 1360w, 1301m, 1202m, 1163w, 1026w, 857m, 804m, 779m, 767m, 707m, 680m, 654m, 563w, 491w. ^{1}H NMR (CDCl$_3$): δ 8.27 (s, N═C*H*, 1H), 7.15−7.40 (m, benzyl-*H*, 5H), 7.14 (br s, aryl-*H*, 2H), 7.02 (d, aryl-*H*, *J* = 2.1 Hz, 1H), 6.85 (br s, aryl-*H*, 1H), 6.80 (br s, aryl-*H*, 1H), 5.24 (s, C*H*, 1H), 4.80 (m, N-C*H*$_2$, 2H), 2.29 (s, Me, 3H), 1.33 (s, ^{t}Bu, 18H), 1.24 (s, ^{t}Bu, 18H), −0.58 (s, Al-C*H*$_3$, 3H), −0.65 (s, Al-C*H*$_3$, 3H), −1.94 (s, Al-C*H*$_3$, 3H). ^{13}C NMR: δ 170.5 (N═*C*H), 150.0 (aryl), 141.4 (aryl), 139.3 (aryl), 138.7 (aryl), 133.9 (aryl), 133.2 (aryl), 132.3 (aryl), 131.8 (aryl), 129.9 (aryl), 129.5 (aryl), 129.4 (aryl), 129.1 (aryl), 127.5 (aryl), 126.5 (aryl), 123.0 (aryl), 121.6 (aryl), 61.7 (N-*C*H$_2$), 58.6 (*C*H), 32.0 (overlapping primary carbons), 32.0 (^{t}Bu), 30.8 (^{t}Bu), 30.4 (^{t}Bu), 20.5 (Me), −9.7 (Al-Me), −11.9 (Al-Me), −13.6 (Al-Me). ^{27}Al NMR (CDCl$_3$): δ 66 $\omega_{1/2}$ 3.2 kHz.

Synthesis of [(6)Al$_3$Me$_6$], 10. (a) A 2.0 M solution of trimethylaluminum in toluene (0.88 mL, 1.76 mmol) was added to a solution of **6**H$_3$ (0.30 g, 0.44 mmol) in toluene (10 mL) at 0 °C. The reaction was allowed to warm to room temperature, stirring overnight. The solvent was removed under vacuum, and the residue was redissolved in a minimum amount of pentane. Storage of the mixture for several days at −30 °C produced a yellow microcrystalline solid. Although predominately **10**, the ^{1}H NMR spectrum of the material indicates that the solid was contaminated with small amounts of **9**.

(b) In an alternative method, a 2.0 M solution of trimethylaluminum (64 μL, 0.13 mmol) was added to a solution of **9** (0.08 g, 0.10 mmol) in 5 mL of toluene. After stirring overnight the solvent was removed, and the residue was redissolved in pentane and stored at −30 °C. As before, the resulting crystalline solid was a mixture of **10** and a small amount of **9**. Repeated attempts to purify **10** were unsuccessful. ^{1}H NMR (CDCl$_3$): δ 8.32 (s, 1H, N═C*H*), 8.02 (s, 1H, C*H*), 7.4−7.1 (m, 10H, aryl), 6.68 (s, 1H, aryl), 4.93 (m, 2H, N-C*H$_2$*), 2.44 (s, 3H, Me), 1.37 (s, 9H, ^{t}Bu), 1.33 (s, 9H, ^{t}Bu), 1.31 (s, 9H, ^{t}Bu), 1.27 (s, 9H, ^{t}Bu), −0.44 (s, 3H, Al-Me), −0.72 (s, 3H, Al-Me), −0.91 (s, 3H, Al-Me), −1.36 (s, 3H, Al-Me), −1.66 (s, 3H, Al-Me), −1.85 (s, 3H, Al-Me).

Synthesis of [(7)Al$_6$Me$_{12}$], 11. In an attempt to improve the synthesis of the trinuclear species, a 2.0 M solution of trimethylaluminum in toluene (1.05 mL) was added to a cooled (0 °C) solution of 0.40 g of **7**H$_3$ (0.35 mmol) in 20 mL of toluene. The yellow mixture was allowed to warm to room temperature and was stirred overnight. The solvent was removed in vacuo, and the residue was redissolved in 2 mL of dichloromethane. The mixture was stored at −30 °C overnight, and the resultant yellow microcrystalline solid was collected, washed with cold dichloromethane, and dried to yield 0.35 g of product. In comparison to the synthesis of **10**, the crystalline solid contains significantly smaller amounts of the impurity [(**7**)Al$_4$Me$_6$]. Yield: 67%. IR (KBr, ν_{max}/cm^{-1}): 3484w, 3125w, 2950s, 2871m, 1621s (C═N stretch), 1580w, 1547w, 1477s, 1436s, 1417w, 1397w, 1362m, 1306m, 1201m, 1156w, 1130w, 1097w, 1039w, 980w, 878m, 817m, 780m, 688s. ^{1}H NMR (CDCl$_3$): δ 8.12 (s, 2H, N═C*H*), 8.04 (s, 2H, C*H*), 7.12, 7.00, 6.89, 6.69 (s, 18 H, Ar-*H*), 4.13 (br, 4H, NC*H$_2$*), 2.38 (s, 6H, C*H$_3$*), 1.34 (s, 36H, ^{t}Bu), 1.19 (s, 36H, ^{t}Bu), −0.27 (s, 12H, Al-C*H$_3$*), −0.53 (s, 6H, Al-C*H$_3$*), −0.70 (s, 6H, Al-C*H$_3$*), −1.45 (br, 12H, Al-C*H$_3$*). ^{13}C NMR (CDCl$_3$): δ 173.3 (N═*C*H), 150.0 (aryl), 140.6 (aryl), 137.6 (aryl), 137.4 (aryl), 134.9 (aryl), 132.2 (aryl), 122.8 (aryl), 57.7 (N-*C*H$_2$), 36.1 (^{t}Bu), 34.4 (^{t}Bu), 32.1 (^{t}Bu), 31.7 (^{t}Bu), 31.3 (*C*H), 20.9 (Me), −5.7 (Al-Me), −6.4 (Al-Me), −8.4 (Al-Me), −9.7 (Al-Me). ^{27}Al NMR (CDCl$_3$): δ 62 $\omega_{1/2}$ 3.1 kHz.

Preparation of [(5){AlMe$_2$}{AlMe(OSMe$_2$)}], 12. A solution of DMSO (11 μL, 0.154 mmol) in CH$_2$Cl$_2$ (1 mL) was added to a solution of **8** (0.10 g, 0.154 mmol) in CH$_2$Cl$_2$ (4 mL), and the mixture was stirred overnight. The volume was reduced to half, and the solution was stored at −30 °C. Crystals formed over several days and were isolated, washed with cold pentane, and dried to yield 0.064 g of product as a yellow solid (58%). Anal. Calcd for $C_{43}H_{57}NAl_2O_4S$: C, 69.99; H, 7.79; N, 1.90. Found: C, 69.89; H, 7.71; N, 1.71. IR (KBr, ν_{max}/cm^{-1}): 3395w, 3131w, 2948s, 2919s, 2861w, 1620s (C═N stretch), 1551s, 1473s, 1443s, 1310m, 1248m, 1177m, 1030w, 991m, 959m, 895m, 869s, 811m, 794m, 684s, 650s, 573w, 496w. ^{1}H NMR (CDCl$_3$): δ 8.05(s, N═C*H*, 1H), 7.59 (s, aryl-*H*, 1H), 7.18−7.34 (m, benzyl-*H*, 5H), 6.82 (s, aryl-*H*, 1H), 6.78 (s, aryl-*H*, 2H), 6.76 (s, aryl-*H*, 2H), 6.01 (s, C*H*, 1H), 4.60 (s, N-C*H*$_2$, 2H), 2.68 (br s, S-C*H*$_3$, 6H), 2.18 (s, Me, 3H), 2.14 (s, Me, 18H), 1.35 (s, ^{t}Bu, 18H), −0.69 (s, Al-C*H*$_3$, 3H), −1.35 (s, Al-C*H*$_3$, 6H). ^{13}C NMR: δ 170.8 (N═*C*H), 165.3 (aryl), 161.5 (aryl), 153.8 (aryl), 138.2 (aryl), 138.1 (aryl), 137.6 (aryl), 136.5 (aryl), 135.4 (aryl), 132.5 (aryl), 131.3 (aryl), 129.1 (aryl), 128.7 (aryl), 125.2 (aryl), 123.5 (aryl), 120.5 (aryl), 118.2 (aryl), 60.4 (N-*C*H$_2$), 37.8 (*C*H), 35.4 (S-Me), 34.3 (S-Me), 35.0 (^{t}Bu), 30.4 (^{t}Bu), 21.4 (Me), 20.9 (Me), −10.6 (Al-Me), −12.7 (Al-Me). ^{27}Al NMR (CDCl$_3$): δ 61 $\omega_{1/2}$ 2.8 kHz.

Preparation of [(5H)$^+$AlMe$^-$], 13. A 0.20 g (0.303 mmol) portion of **8** was dissolved in methylene chloride (5 mL) and cooled to −30 °C. In a separate flask, the desired ketone (cyclopentanone: 52.0 μL, 0.606 mmol or cyclohexanone: 49.4 μL, 0.606 mmol) was dissolved in 2 mL of methylene chloride and cooled to −30 °C. The two chilled solutions were mixed and allowed to stir at room temperature for 12 h. The volume of methylene chloride was reduced to ca. 2 mL, and the mixture was stored at −30 °C until a crystalline solid formed. The solid was isolated and dried to yield 0.10 g of yellow crystals (52%). Anal. Calcd for $C_{39}H_{46}NAlO_3$: C, 77.58; H, 7.68; N, 2.32. Found: C, 77.19; H, 7.51; N, 2.06. IR (KBr, ν_{max}/cm^{-1}): 3477w (N−H stretch), 3145w, 2949s, 2923m, 2865m, 1647s (C═N stretch), 1626m, 1556m, 1470s, 1443s, 1404m, 1352m, 1290m, 1256m, 1202m, 1032w, 861m, 801m, 698m, 659m, 550w, 497w. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.93 (d, N═C*H*, *J* = 14.4 Hz, 1H), 7.52 (d, aryl-*H*, *J* = 1.8 Hz, 1H), 7.34−7.48 (m, benzyl-*H*, 5H), 7.32 (d, aryl-*H*, *J* = 2.1 Hz, 1H), 6.96 (br s, *H*N═C, 1H), 6.92 (d, aryl-*H*. ^4J = 2.0 Hz, 2H), 6.81 (d, aryl-*H*, *J* = 1.9 Hz, 2H), 5.12 (s, C*H*, 1H), 4.73 (d, N−C*H$_2$*, *J* = 5.4 Hz, 2H), 2.24 (s, Me, 3H), 2.16 (s, Me, 6H), 1.33 (s, ^{t}Bu, 18H), −0.80 (s, Al-C*H$_3$*, 3H). ^{13}C NMR: δ 166.1 (N═*C*H), 157.2 (aryl), 145.0 (aryl), 139.8 (aryl), 137.7 (aryl), 134.0 (aryl), 132.3 (aryl), 132.0 (aryl), 131.4 (aryl), 130.2 (aryl), 130.1 (aryl), 129.6 (aryl), 129.2 (aryl), 126.9 (aryl), 125.8 (aryl), 116.3 (aryl), 59.4 (N-*C*H$_2$), 56.2 (*C*H), 35.2 (^{t}Bu), 30.3 (^{t}Bu), 20.8 (Me), 20.2 (Me), −13.3 (Al-Me). ^{27}Al NMR (CD$_2$Cl$_2$): δ 61 $\omega_{1/2}$ 3.2 kHz.

Preparation of [(6H)$^+$AlMe$^-$], 14. A 0.20 g (0.269 mmol) portion of **9** was dissolved in methylene chloride (5 mL) and cooled to −30 °C. In a separate flask, the desired ketone (cyclopentanone: 46.0 μL, 0.538 mmol; cyclohexanone: 45.8 μL, 0.538 mmol) was dissolved in 2 mL of methylene chloride and cooled to −30 °C. The two cooled solutions were mixed and allowed to stir at room temperature for 12 h. The methylene chloride solvent was reduced to ca. 2 mL and stored at −30 °C until a crystalline solid formed. The solid was isolated and dried to yield 0.18 g of a yellow solid (66%). Anal. Calcd for $C_{45}H_{58}NAlO_3 \cdot 1/2CH_2Cl_2$: C, 75.06; H, 8.17; N, 1.93. Found: C, 75.57; H, 7.48; N, 2.25. ^{1}H NMR (CD$_2$Cl$_2$): δ 8.02 (d, N═C*H*, *J* = 14.3 Hz, 1H), 7.37 (br s aryl-*H*, 1H),7.28−7.40 (m, benzyl-*H*, 5H), 7.26 (br s, aryl-*H*, 1H), 7.07 (d, aryl-H, *J* = 2.1 Hz, 2H), 7.01 (br s, *H*N═C, 1H), 6.90 (d, aryl-*H*, *J* = 1.8 Hz, 2H), 5.11 (s, C*H*, 1H), 4.72 (d, N−CH$_2$, *J* = 5.3 Hz, 2H), 2.16 (s, Me, 3H), 1.25 (s, ^{t}Bu, 18H), 1.17 (s, ^{t}Bu, 18H), −0.88 (s, Al-C*H*$_3$, 3H). ^{13}C NMR: δ 166.4 (N═*C*H), 157.1 (aryl), 145.2 (aryl), 139.2 (aryl), 139.1 (aryl), 138.0 (aryl), 134.0 (aryl), 132.2 (aryl), 131.3 (aryl), 130.3 (aryl), 130.2 (aryl), 129.7 (aryl), 129.4 (aryl), 127.7 (aryl), 123.4 (aryl), 116.5 (aryl), 60.4 (N-*C*H$_2$), 56.3

(*C*H), 35.6 (^{t}Bu), 34.4 (^{t}Bu), 32.0 (^{t}Bu), 30.3 (^{t}Bu), 20.2 (Me), −12.7 (Al-Me).

X-ray Crystallography. Unit cell dimensions and intensity data for all the structures are contained in Table 1. The data were obtained on a Siemens CCD SMART diffractometer at −100 °C, with monochromatic Mo Kα X-rays ($\lambda = 0.71073$ Å). The data collections nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different ϕ angle for the crystal, and each exposure covered 0.3° in ω. The crystal to detector distance was 5.0 cm. The data sets were corrected empirically for absorption using SADABS.[38] All the structures were solved using the Bruker SHELXTL software package for the PC, using the direct methods option of SHELXS. The space groups for all of the structures were determined from an examination of the systematic absences in the data, and the successful solution and refinement of the structures confirmed these assignments. Except for the phenolic hydrogen atoms and hydrogen atoms involved in H-bonding interactions, all hydrogen atoms were assigned idealized locations and were given a thermal parameter equivalent to 1.2 or 1.5 times the thermal parameter of the carbon atom to which it was attached. For the methyl groups, where the location of the hydrogen atoms was uncertain, the AFIX 137 card was used to allow the hydrogen atoms to rotate to the maximum area of residual density, while fixing their geometry. In several cases, the crystals contained severely disordered solvate molecules, and in instances where a suitable model could not be constructed for the solvates, their contribution to the diffraction were removed ("squeezed") from the data by the Platon for Windows software program.[39] Experimental details are contained in the Supporting Information.

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Supporting Information Available: Complete crystallographic information (excluding structure factors) for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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