Synthesis and Reactivity of Bi-, Tri-, and Tetrametallic Aluminum Tetraphenolate Complexes

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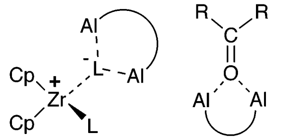
A series of ligands, each with four phenoxide arms, have been prepared with the intent to place two Lewis acidic metal center in close proximity and thus foster cooperative binding of external Lewis bases. The ligands **1**−**5** incorporate a pair of 2,2′-methylenebis(4-*tert*-butyl-6-alkylphenol) groups linked by three different spacers: anthracene (**1**H_4, **5**H_4), dibenzofuran (**2**H_4, **4**H_4), and xanthene (**3**H_4). The reaction of **1**H_4 and **2**H_4 with trimethylaluminum led to the formation of the C_2-symmetric, tetranuclear aluminum compounds [(**1**)Al_4Me_8], **6**, and [(**2**)Al_4Me_8], **7**, respectively. In contrast, when **3**H_4 was treated with trimethylaluminum, a binuclear aluminum species, [(**3**)Al_2Me_2], **8**, containing an Al_2O_2 bridging unit, was isolated. Heating solutions of the tetranuclear complexes **6** and **7** in the presence of excess ligand induced the elimination of 2 equiv of trimethylaluminum and afforded the binuclear aluminum complexes [(**1**)Al_2Me_2], **9**, and [(**2**)Al_2Me_2], **10**. Addition of NEt_4Cl to solutions of **9** and **10** resulted in the isolation of the anionic, bimetallic aluminum species [NEt_4][(**1**)Al_2Me_2Cl], **11**, and [NEt_4][(**2**)Al_2Me_2Cl], **12**. Both complexes contain a symmetrical chloride bridge between the two metal centers. In contrast, the reaction of NEt_4Cl with **8** produced the asymmetric dianionic compound [NEt_4]$_2$[(**3**)$Al_2Me_2Cl_2$], **13**. Compound **9** reacts with sodium phenoxide to afford [(**1**)Al_2Me_2(OPh)Na(OEt_2)], **14**, and this species contains a six-membered $NaAl_2O_3$ ring. When ketones or aldehydes are added to **9**, the two aluminum centers in the resulting product each bind a carbonyl group in an η^1 fashion. For example, the reaction of α,α,α-trimethylacetophenone with **9** produced the C_2-symmtetric complex {(**1**)[AlMe($OC_{11}H_{14}$)]$_2$}, **15**, while **10**, upon addition of cyclopentanone, afforded the asymmetric, monometallic species [(**2**H)Al(OC_5H_8)], **16**, with one free phenolic arm. The three remaining phenoxide groups in **16** all coordinate to the lone aluminum. To probe the influence of the steric environment of the ligand on the reactivity, methyl groups were incorporated at the *ortho*-position of the phenoxide, and this ligand, **4**H_4, reacted with trimethylaluminum to produce the trinuclear species [(**4**)Al_3Me_5], **17**, with a stabilizing six-membered Al_3O_3 bridge. The slightly more sterically encumbered isopropyl-substituted ligand, **5**H_4, formed the binuclear aluminum species [(**5**)Al_2Me_2], **18**, analogous to **8**, **9**, and **10**. Addition of benzaldehyde to **18** afforded the asymmetric binuclear species {(**5**)[AlMe][AlMe(OCHPh)]}, **19**, and the benzaldehyde substrate coordinates to only one aluminum in this complex.

Introduction

Multidentate Lewis acids have utility in many important areas of chemistry including organic catalysis and anion complexation.[1] Binuclear Lewis acidic systems are particularly noteworthy in view of their potential to interact simultaneously with a single substrate. With two Lewis acidic metals simultaneously accepting electron density from a single substrate, the resulting complex should exhibit enhanced reactivity (Scheme 1). To date, relatively few examples of well-defined, binuclear Lewis acidic complexes have been reported, and in only a few of these cases, the two Lewis acid sites bind a single external Lewis base (i.e., carbonyl group).[1,2] Most of the research effort in bimetallic Lewis acids has been focused on anionic sequestration[3−6] or utilized mercury, a relatively soft Lewis acid.[1b,2,7−9] With harder Lewis acids such as aluminum, the coordination of a substrate in a cooperative manner by the two metal centers should result in the generation of an extremely reactive species with the ability to catalyze unusual organic transformations. This type of interaction has been invoked to explain the reactivity of several aluminum complexes but has never been

Scheme 1



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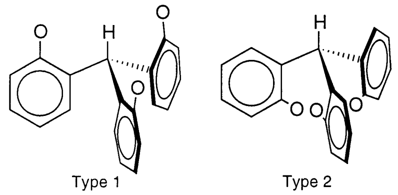
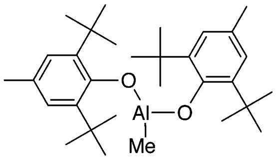
proven.[10] In addition, bifunctional Lewis acidic assemblies may have the ability to remove anionic ligands such as chloride or alkyl groups from transition metals, affording cationic catalysts useful in olefin polymerizations.[11,12] Indeed, sterically encumbered anionic, bimetallic cocatalysts should be more efficient anion sequestering agents compared to their mononuclear analogues, and they have the potential to enhance polymerization activity and molecular weights by restricting the interaction between the two ionic species.[11,12] Unfortunately, the isolation and identification of discrete catalytic species with hard Lewis acids, such as aluminum, has remained quite elusive. For example, most attempts to prepare bifunctional species with phenoxide ligands have been hindered by the ability of phenoxides to serve as bridging ligands in conjunction with the propensity of aluminum to adopt tetrahedral stereochemistry.[13] The reaction of hard Lewis acids (e.g., aluminum) with oxygenated species typically affords products with two independent mononuclear η^1 interactions. Presumably, the significantly smaller $\Delta H°$ for coordination of the second carbonyl lone pair relative to the first favors the η^1-binding of a carbonyl substrate to each Lewis acid site, unless the carbonyl group is incorporated directly in the ligand backbone.[14]

Scheme 2



With these issues in mind, we have developed a simple strategy for the preparation of a tetraphenolic ligand system with tunable attributes. Given the effectiveness of “designer Lewis acids” such as methyl aluminum 2,6-di-*tert*-butyl-4-methylphenolate (MAD)[15] for organic transformations, we chose to link two sets of bulky 2,2′-methylenebis(4,6-di-alkylphenol) groups with a flat, aromatic spacer. If the two sets of bisphenol arms were to each bind an aluminum alkyl, we reasoned that the coordination sphere of the metals in the resulting complex should resemble MAD, and modifications in the aromatic spacer would then allow the distance between the two aluminums to be adjusted. Since phenols joined at the 2-position tend to align together with respect to hydrogen on the linking carbon,[16−18] the two sets of 2,2′-methylenebis(4,6-dialkylphenol) groups in a bimetallic complex should be directed toward each other if large bulky groups are placed at the *para*-position of the phenoxides. Herein, we report the isolation and characterization of a series of reactive bi-, tri-, and tetranuclear aluminum complexes incorporating these teteraphenolic ligands. The reactivity of the binuclear species with external Lewis bases is also discussed.



MAD

Results and Discussion

When two or more phenol groups are linked at the 2-position to a common methine carbon, two extreme conformations can be envisaged wherein the oxygen atoms either align with respect to the methine hydrogen, Type 1, or orient away from this atom, Type 2. In our work with tris(3,5-dialkyl-2-hydroxyphenyl)methane ligands, a profound tendency for the trisphenolic arms to adopt the Type 1 configuration has been noted, although in certain instances the ligands adopt a type 2 geometry (Scheme 2).[19] The preference for the Type 1 geometry appears to be primarily a steric effect, and in

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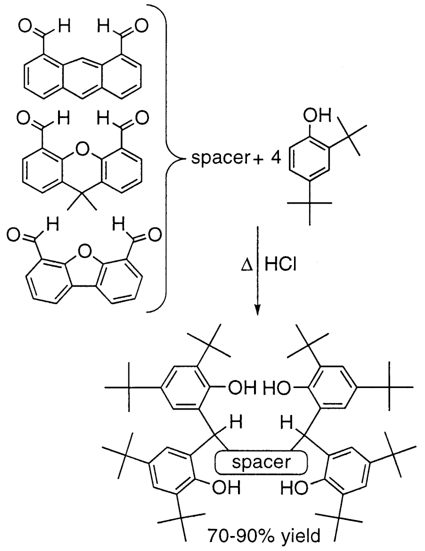
Scheme 3



light of this unique preference for the arms to align, a simple strategy was devised to prepare a tetraphenolic ligand system predisposed to bind two metal centers. As outlined in Scheme 3, the addition of 4 equiv of 2,4-di-*tert*-butylphenol to aromatic spacers containing two reactive aldehydes (1,8-anthracenedicarboxaldehyde, 4,6-dibenzofurandicarboxaldehyde, and 4,5-diformyl-9,9-dimethylxanthene) affords the tetraphenolic ligands 4,4′,4″,4‴-tetra-*tert*-butyl-6,6′,6″,6‴-tetra-*tert*-butyl-2,2′,2″,2‴-(1,8-anthracenemethanediyl)tetraphenol (**1**H_4), 4,4′,4″,4‴-tetra-*tert*-butyl-6,6′,6″,6‴-tetra-*tert*-butyl-2,2′,2″,2‴-(4,6-dibenzofuranmethanediyl)tetraphenol (**2**H_4), and 4,4′,4″,4‴-tetra-*tert*-butyl-6,6′,6″,6‴-tetra-*tert*-butyl-2,2′,2″,2‴-(4,5-methanediyl-9,9-dimethylxanthene)tetraphenol (**3**H_4) in high yields.[20] In each case, the ligands contain two distinct sets of 2,2′-methylenebis(4,6-di-*tert*-butylphenol) groups linked by different spacers, and the incorporation of sterically encumbering *tert*-butyl groups at the *para*-positions of the phenolic donors forces the arms to orient toward each other in order to reduce unfavorable steric interactions. Thus, if two metal centers can be integrated into the ligand system, their proximity should allow them to interact in concert with a common substrate. An initial report outlining the properties of **1**H_4 and the aluminum complexes prepared with it was recently communicated.[21]

With the capacity to substitute different linkers between the two sets of 2,2′-methylenebis(4,6-di-*tert*-butylphenol) groups, the spacing and orientation of the ligands can be tuned to produce bimetallic metal complexes with the desired properties. For instance, a survey of the solid-state structures of compounds **1**H_4, **2**H_4, and **3**H_4 indicates the average distance between the methine carbons varies with regard to the spacer: dibenzofuran (5.5 Å), anthracene (5.1 Å), and xanthene (4.3 Å). The utilization of a fused ring system as the basic backbone of the ligand should hinder significant reorientation of the donor groups upon formation of the metal complexes, a common problem in the development of bimetallic Lewis acid catalysts.[13]

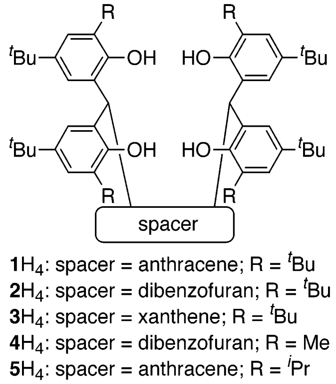


Figure 1. Depiction of the tetraphenolic ligands utilized in this investigation.

In addition to the ability to interchange spacers, the steric attributes of the metal binding pocket can be adjusted by the substitution of different alkyl groups at the 2-position of the phenolic precursors, and as long as the 4-position contains a *tert*-butyl group, the two sets of oxygen donors should point directly at each other. Accordingly, the less bulky 4,4′,4″,4‴-tetra-*tert*-butyl-6,6′,6″,6‴-tetramethyl-2,2′,2″,2‴-(4,6-dibenzofuranmethanediyl)tetraphenol (**4**H_4) and 4,4′,4″,4‴-tetra-*tert*-butyl-6,6′,6″,6‴-tetra-isopropyl-2,2′,2″,2‴-(1,8-anthracenemethanediyl)tetraphenol (**5**H_4) were synthesized (Figure 1). As discussed for **1**H_4, the steric strain caused by the *tert*-butyl groups induces a distortion in the anthracene spacer, and the substitution of the isopropyl groups for the *tert*-butyls in the *ortho*-position of the phenolic donors reduces the twist [defined as the angle between the planes C(15),C(30),C(31) and C(44),C(34) C(33)] in the spacer from 38.5° in **1**H_4 (Figure 2) to 16.9° in **5**H_4 (Figure 3) [angle between the planes C(14),C(28),C(29) and C(42),C(32),C(31)]. In contrast to the anthracene linker in **1**H_4 and **5**H_4, the dibenzofuran backbones in **2**H_4 and **4**H_4 are almost perfectly flat, and in general, a greater deviation from planarity has been noted for the anthracene spacer relative to dibenzofuan. The two aromatic carbon atoms between the outer phenyl rings in the anthracene spacer allow these rings to flex relative to each other. Dibenzofuran has only a single oxygen atom between these two outer phenyl groups and is thus much less pliable. In the eight structurally characterized examples of compounds with the anthracene spacer presented in this study (vide infra), the angles between the planes as defined above range from 4.5° to 45.7° (mean value 25.5°; SD 14.7°), while the angles between the analogous planes in the seven complexes that contain dibenzofuran vary only from 4.3° to 15.2° (mean value 9.0°; SD 3.9°). With an aliphatic carbon atom linking the two outer phenyl rings, the xanthene also exhibits extensive deviations (>41°) from planarity.

Synthesis of Tetranuclear Aluminum Complexes. Regardless of the number of equivalents of trimethylaluminum added to the mixture, initial reactions of **1**H_4 afforded a complex containing four aluminum centers, **6**. Four distinct resonances arising from Al-CH_3 groups could be identified in the ^{13}C and ^{1}H NMR spectra of the product. Compound **2**H_4 appeared to react analogously with trimethylaluminum, and the product, **7**, was

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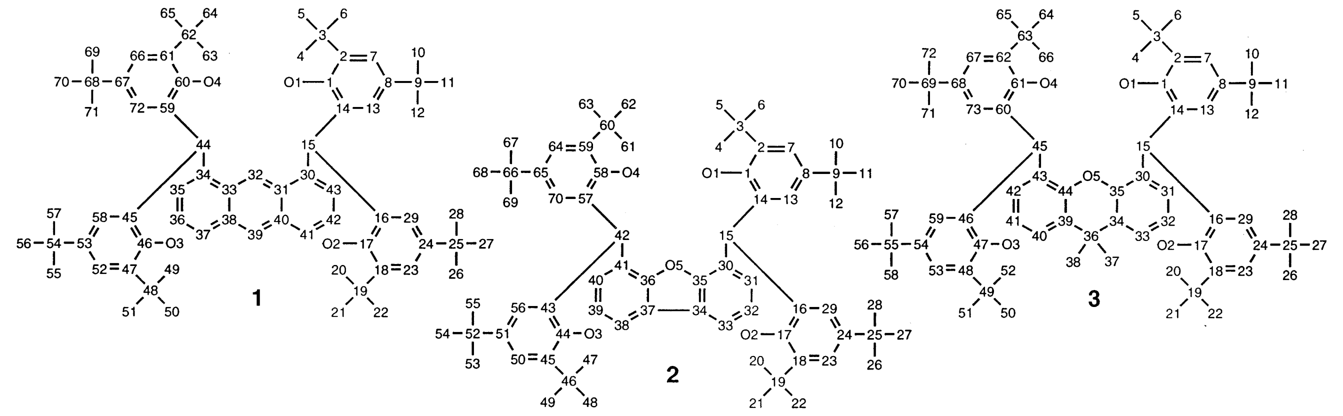

Figure 2. Atom-numbering scheme for ligands **1**, **2**, and **3**.

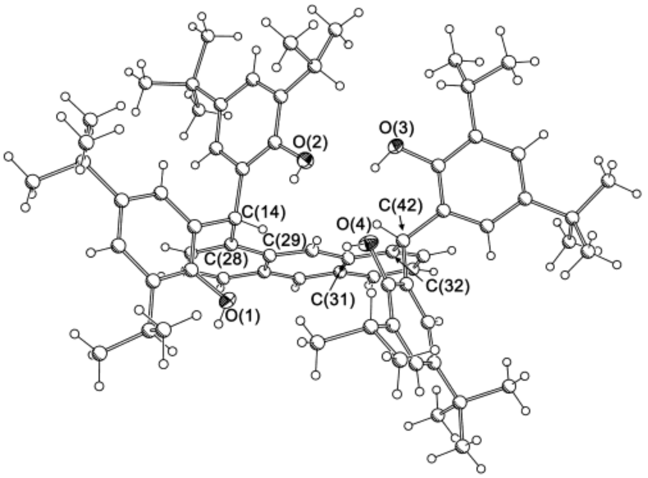

Figure 3. Diagram of the structure of **5** (30% probability ellipsoids for oxygen atoms; carbon atoms drawn with arbitrary radii).

characterized by X-ray crystallography (Scheme 4; Figure 4; Tables 1 and 2). Both **6** and **7** are C_2 symmetric in the solid state and in solution, and each set of 2,2′-methylenebis(4,6-di-*tert*-butylphenol) groups appears to have reacted with one bridging and one terminal methyl group from an Al_2Me_6 molecule. In both **6** and **7**, each pair of aluminum centers are joined by a phenolic oxygen in addition to one bridging methyl group. Interestingly, in the presence of excess ligand, **6** will continue to react slowly over a period of a few days at room temperature to afford a new species, while, in contrast, complex **7** demonstrated no tendency to react further unless the solution was heated. Given that the phenolic arms are identical in the two ligands, the disparity in reactivity may be attributed to a combination of either the increased flexibility of **1**H_4 in comparison to **2**H_4 or the variation in the separation of the two sets of 2,2′-methylenebis(4,6-di-*tert*-butylphenol) groups. Since the focus of the project was the preparation of bifunctional Lewis acid assemblies, no further attempts to isolate the analogous tetranuclear species for **3**, **4**, and **5** were undertaken.

Compounds **6** and **7** both exhibit several unique structural features. Although most of the metal carbon distances are comparable to Al_2Me_6, inclusion of a phenolic group between the metal centers induces pronounced asymmetry in the methyl bridge, with distances in **6** of 2.066(6) and 2.163(6) Å to Al(1) and Al(2), respectively. The analogous bonds in **7** are 2.086(6) and 2.150(6) Å. Additionally, the phenoxide bridge increases the Al(1)−Al(2) separation to 2.7570(19) Å in **6** and 2.715(2) Å in **7** relative to the values found in Al_2Me_6 (X-ray −2.606(2) Å; neutron −2.700(10) Å).[22] Despite the complexity of the tetranuclear structure, both linkers are reasonably flat relative to the plane defined by C(15),C(30),C(31) and C(42),C(41),C(36). An angle of 9.6° is observed in the dibenzofuran linker in **7**, while **6** exhibits a minor distortion of 4.5° in the anthracene backbone.

Synthesis of Binuclear Lewis Acid Assemblies. Although both **1**H_4 and **2**H_4 form tetrametallic complexes upon addition of trimethylaluminum, all attempts to react **3**H_4 in a similar manner produced a species that exhibited a single Al-methyl resonance in the ^1H NMR spectrum. This C_2-bimetallic complex, **8**, was obtained as a highly crystalline material directly from the reaction mixture upon cooling to −35 °C. As depicted in Figure 5 and Scheme 4, each of the 2,2′-methylenebis(4,6-di-*tert*-butylphenol) groups has reacted with two alkyl groups from one $AlMe_3$ group, and rather than adopting a structure similar to the three coordinate MAD species, two of the phenolic oxygen atoms have bridged the two aluminum centers, allowing the formation of a stable Al_2O_2 unit while adopting the preferred tetrahedral coordination geometry for the metals.[23,24] Crystallographic data can be found in Tables 1 and 3. Although the Al_2O_2 unit is rigidly planar with the sum of the angles totaling 359.9(1)°, its formation comes at the expense of a severe distortion in the xanthene linker, exemplified by the 41.7° angle between the planes defined by C(15),C(30),C(35) and C(45),C(43),C(44). With this deformation, the aluminum centers in the Al_2O_2 unit are situated 2.8079(19) Å from each other, and the other structural parameters are unexceptional.

All attempts to isolate the tetranuclear complex analogous to **6** and **7** with **3** were unsuccessful even at

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Table 1. X-ray Structural Data[a] for Compounds $5H_4$−11

	$5H_4$·3OCMe$_2$	**6**·2C_5H_{12}	**7**·3CH_2Cl_2	**8**·3CH_2Cl_2	**9**·3C_5H_{12}	**10**·C_5H_{12}·CH_2Cl_2	**11**·C_5H_{12}·CH_2Cl_2
total no. of reflns	19 250	22 127	42 749	44 504	18 990	33 009	45 513
no. of unique reflns	11 705	13 827	13 377	13 646	11 472	9926	14 664
R(int)	0.0452	0.0816	0.0993	0.1054	0.0868	0.0790	0.0437
θ_{max} (deg)	24.74	24.00	24.00	25.00	23.00	22.50	25.00
chem formula	$C_{77}H_{104}O_7$	$C_{90}H_{138}O_4Al_4$	$C_{81}H_{118}O_5Al_4Cl_6$	$C_{78}H_{106}O_5Al_2Cl_6$	$C_{89}H_{132}O_4Al_2$	$C_{78}H_{104}O_5Al_2Cl_2$	$C_{87}H_{128}O_4Al_2Cl_3N_1$
fw	1141.60	1391.92	1492.37	1390.29	1319.91	1246.47	1412.21
cryst syst	triclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
μ(Mo Kα) (mm^{-1})	0.069	0.098	0.289	0.291	0.082	0.155	0.178
a (Å)	13.3480(8)	13.6213(7)	16.1000(11)	14.7565(18)	13.652(4)	14.5373(10)	15.1245(7)
b (Å)	16.5313(10)	17.3859(9)	20.8304(14)	43.043(5)	15.532(5)	23.7780(17)	21.2736(10)
c (Å)	17.2102(10)	21.1789(11)	26.6007(18)	13.4321(16)	21.088(6)	22.6129(16)	26.0590(11)
α (deg)	80.230(1)	111.891(1)			72.037(5)		
β (deg)	73.329(1)	98.218(1)	107.3370(10)	114.592(2)	77.508(6)	103.481(2)	95.246(1)
γ (deg)	71.513(1)	101.501(1)			82.443(6)		
V_c (Å^3)	3437.3(4)	4428.3(4)	8515.8(10)	7557.8(16)	4143(2)	7601.2(9)	8349.4(7)
Z	2	2	4	4	2	4	4
R_1 [$I \geq 2\sigma(I)$ data][b]	0.0622 [5861]	0.0912 [8243]	0.0914 [8210]	0.0878 [7097]	0.0890 [7699]	0.0668 [4998]	0.0660 [10122]
wR_2 (all data)[c]	0.1705	0.2510	0.2354	0.2104	0.2480	0.1910	0.2004
largest diff peak, hole (e Å^{-3})	0.373, −0.250	0.369, −0.508	0.464, −0.392	0.424, −0.760	0.583, −0.310	0.751, −0.332	0.907, −0.434

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

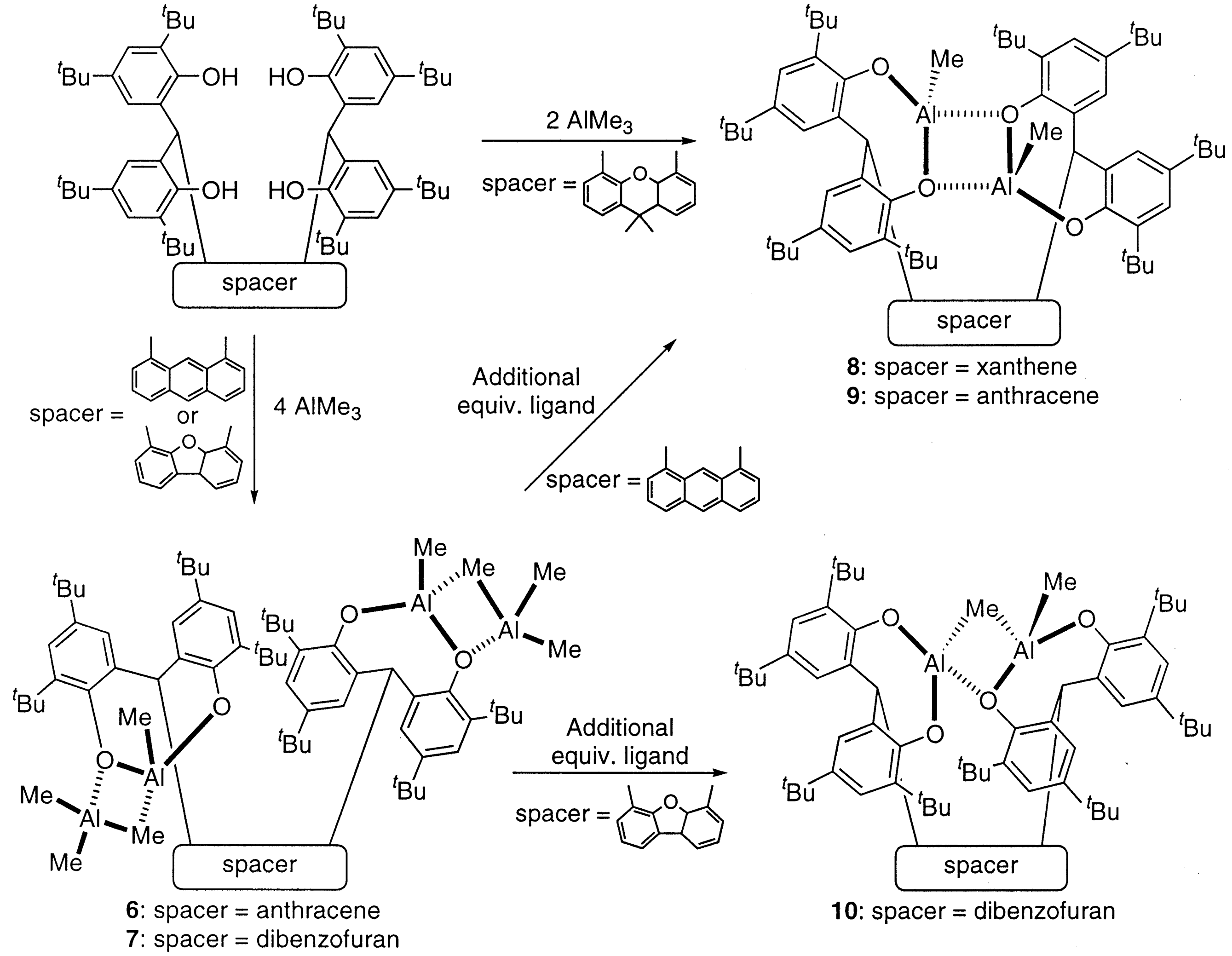
0 °C. The distance between the two sets of phenoxide donor groups is significantly shorter with the xanthene spacer, and apparently, there may not be sufficient room to form the tetranuclear species. The small separation in this flexible spacer instead favors the formation of the familiar Al_2O_2 bridge.

Although they contain a different number of metal centers, closer inspection of the solid-state structures reveals that the orientations of the ligands in **6** and **8** are quite similar; complex **6** simply has two additional trimethylaluminum units attached to its periphery, concomitant with disruption of the phenoxide bridges. Indeed, heating a solution of **6** for a brief period in the presence of an additional equivalent of the ligand induced the liberation of 2 equiv of trimethylaluminum and formation of a bimetallic species, **9**, in high yield (Scheme 4). Crystallographic studies have demonstrated that **9** adopts a structure analogous to **8**, although the Al−O distances in **9** are marginally longer (on average 0.02 Å), and subsequently, the metal−metal separation increases slightly to 2.834(2) Å (Figure 6, Table 3).[21] Surprisingly, whereas the Al_2O_2 core structure is nearly identical in both complexes, the distance between the methine carbon atoms linking the phenoxide donors increases markedly from 4.159 Å in **8** to 4.754 Å in **9**. Along with this increase in separation, the backbone distortion decreases somewhat from 41.7° to 31.8° [planes C(15),C(30),C(31) and C(44),C(34),C(33)] in **9**.

In contrast to the ease with which the bimetallic species **8** and **9** form, the conversion of **7** with the dibenzofuran linker into a binuclear species, **10**, was much more problematic and required prolonged heating of a toluene solution of the complex in the presence of excess ligand (Scheme 4). The features of the ^{1}H and ^{13}C NMR spectra of **10** were decidedly more complex in comparison to those of **8** or **9**, and two signals attributed to Al-Me groups were evident. In agreement with the solution data, compound **10** contains an asymmetric four-membered Al−Me−Al−O bridge in the solid state (Figure 7, Tables 1 and 3), where, unlike **8** and **9**, both a phenoxide arm and a methyl group bridge the two aluminum centers. Apparently, the formation of this asymmetric four-membered ring induces a distortion of 15.2° in the usually rigid dibenzofuran plane defined by C(15),C(30),C(35) and C(42),C(41),C(36), and though this twist may not appear to be extremely large when compared to similar measurements in the anthracene and xanthene analogues, this structural feature seems noteworthy given the absence of extended conjugation (anthracene) or the incorporation of a flexible aliphatic center (xanthene). As previously witnessed in both **6** and **7**, the bridging methyl group, C(71), binds asymmetrically to the aluminum centers with distances of 2.058(6) and 2.109(6) Å to Al(1) and Al(2), respectively, and at 2.671(2) Å, the aluminum−aluminum separation is quite short. There is also a small but perceptible variation in the bond distances of the bridging phenoxide, O(3), as well (Al(1)−O(3) 1.806(3) Å and Al(2)−O(3) 1.864(3) Å). Unlike the symmetrical, planar, four-membered Al_2O_2 unit in **8** and **9**, the Al−Me−Al−O bridge is slightly puckered, with a sum of angles totaling 356.6(6)°.

Reaction of Bimetallic Complexes with Anionic Substrates. Even though the aluminum centers in the

Scheme 4



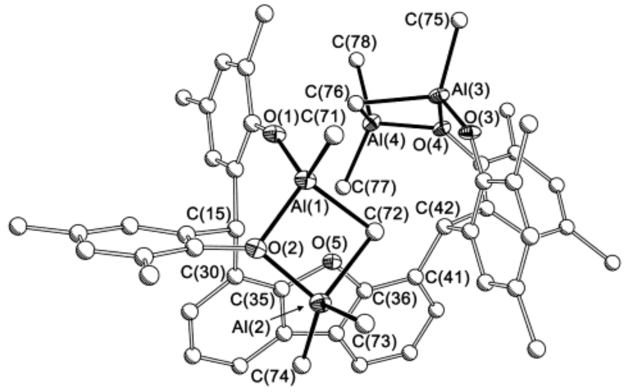


Figure 4. Diagram of the structure of **7** (30% probability ellipsoids for aluminum and oxygen atoms; carbon atoms drawn with arbitrary radii). Bonds to the aluminum atoms are indicated with solid lines. For clarity, the *tert*-butyl methyl groups, and all hydrogen atoms have been omitted.

bimetallic complexes **8**, **9**, and **10** all adopt a tetrahedral structure with a four-membered bridge, the strain induced in the linker groups suggested that they might still be reactive. If the bridging interactions between the two metal centers in **9** and **10** could be disrupted by the addition of external reagents, the resulting bimetallic species would contain two three-coordinate Al(phenoxide)$_2$Me groups quite similar to the structure of the powerful Lewis acid catalyst MAD (Scheme 5), and due to the proximity of the aluminum centers, we reasoned they could potentially coordinate a Lewis base simultaneously. Accordingly, the reactivity of the complexes was probed with a variety of reagents in an attempt to achieve this cooperative binding.

Since bulky bifunctional Lewis acids have the potential to abstract a chloride or methyl group from organometallic species to form reactive catalysts,[11,12] chloride ion was chosen as the first Lewis base. When **9** and **10** were reacted with NEt$_4$Cl in a pentane/dichloromethane (4:1) mixture, a white solid precipitated from solution over a period of 24 h. Unlike all of the aluminum complexes described above, the products were pentane insoluble, and the ^{1}H and ^{13}C NMR spectra suggested that the compounds maintained a high degree of symmetry. Moreover, integration of the spectra indicated that the ratio of Al-Me groups to tetraethylammonium cations was 2:1. Diffusion of pentane into saturated dichloromethane solutions afforded single crystals of **11** (anthracene spacer) and **12** (dibenzofuran), and the solid-state structure of **12** is illustrated in Figure 8. Selected crystallographic parameters can be found in Tables 1, 4, and 5. In both **11** and **12**, the addition of chloride anion has disrupted the bridging unit by situating itself between the two metal centers. Both Lewis acids in the bimetallic complex have coordinated

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Tetrametallic Compounds 6 and 7

6		7	
Bond Lengths (endocyclic distances)			
Al(1)−O(2)	1.859(3)	Al(1)−O(2)	1.855(3)
Al(1)−C(78)	2.066(6)	Al(1)−C(72)	2.086(6)
Al(2)−O(2)	1.850(3)	Al(2)−O(2)	1.854(3)
Al(2)−C(78)	2.163(6)	Al(2)−C(72)	2.150(6)
Al(1)⋯Al(2)	2.7570(19)	Al(1)⋯Al(2)	2.715(2)
Al(3)⋯Al(4)	2.742(2)	Al(3)⋯Al(4)	2.716(2)
Bond Lengths (exocyclic distances)			
Al(1)−O(1)	1.705(3)	Al(1)−O(1)	1.700(3)
Al(1)−C(77)	1.930(5)	Al(1)−C(71)	1.942(5)
Al(2)−C(79)	1.943(5)	Al(2)−C(73)	1.940(5)
Al(2)−C(80)	1.939(5)	Al(2)−C(74)	1.940(6)
Bond Angles (endocyclic angles)			
Al(2)−O(2)−Al(1)	96.05(14)	Al(2)−O(2)−Al(1)	94.09(15)
O(2)−Al(1)−C(78)	91.98(19)	O(2)−Al(1)−C(72)	92.1(2)
O(2)−Al(2)−C(78)	89.21(18)	O(2)−Al(2)−C(72)	90.1(2)
Al(1)−C(78)−Al(2)	81.35(19)	Al(1)−C(72)−Al(2)	79.7(2)
Bond Angles (exocyclic angles)			
O(1)−Al(1)−O(2)	112.16(15)	O(1)−Al(1)−O(2)	110.39(16)
O(1)−Al(1)−C(77)	111.9(2)	O(1)−Al(1)−C(71)	112.6(2)
O(2)−Al(1)−C(77)	115.17(19)	O(2)−Al(1)−C(71)	116.69(19)
O(1)−Al(1)−C(78)	113.9(2)	O(1)−Al(1)−C(72)	113.3(2)
C(77)−Al(1)−C(78)	110.3(3)	C(71)−Al(1)−C(72)	110.3(2)
O(2)−Al(2)−C(79)	112.1(2)	O(2)−Al(2)−C(73)	112.5(2)
O(2)−Al(2)−C(80)	113.5(2)	O(2)−Al(2)−C(74)	113.0(2)
C(78)−Al(2)−C(80)	113.9(3)	C(72)−Al(2)−C(74)	114.7(3)
C(79)−Al(2)−C(80)	120.0(2)	C(73)−Al(2)−C(74)	120.2(3)
C(78)−Al(2)−C(79)	103.5(2)	C(72)−Al(2)−C(73)	101.8(3)

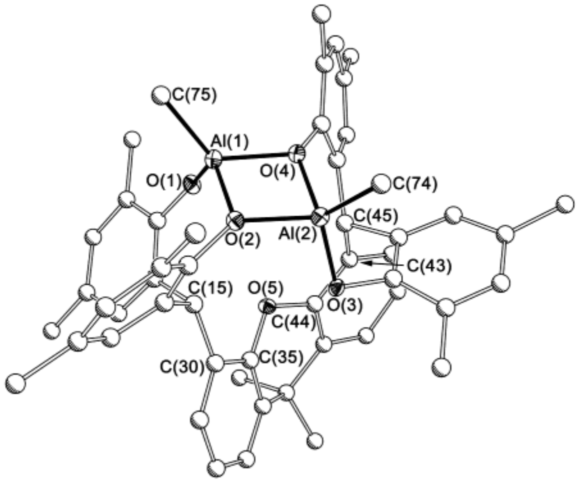


Figure 5. Diagram of the structure of **8** (30% probability ellipsoids for aluminum and oxygen atoms; carbon atoms drawn with arbitrary radii). Bonds to the aluminum atoms are indicated with solid lines. The *tert*-butyl methyl groups and all hydrogen atoms have been omitted for clarity.

simultaneously an external substrate, and these complexes are rare, well-defined examples of this type of transformation (Scheme 6). The geometry about the aluminum sites in **12** is much closer to an idealized tetrahedron in comparison to the starting material **10** with the exception of the angle of 93.68(11)° defined by O(4)−Al(2)−Cl(1). Similar measurements in the anthracene derivative, **11**, disclose a range of angles about the metal center from 98.69(7)° to 119.75(14)°. To accommodate the chloride atom, the Al⋯Al separation in **11** has increased by more than 1 Å relative to **9** to a distance of 3.9886(12) Å. An even larger deformation is evident in the conversion of **10** to **12**. The Al⋯Al distance increases from 2.671(2) Å in the Al−Me−Al−O unit in **10** to 3.9189(18) Å in **12**. Once again, the anthracene backbone in **11** is significantly distorted from planarity, and the angle between the planes defined by the methine carbons has increased considerably relative to **9** to a value of 45.7°. Conversely, the incorporation of the chloride anion significantly alleviates the strain in the dibenzofuran linker from 15.2° in **10** to 4.3° in **12**. The remaining geometric parameters in the complex are unremarkable except for a minor shortening of the Al−Cl distances from 2.3139(11) and 2.3224(11) Å in **11** to 2.2695(17) and 2.3011(16) Å in **12**. Nonetheless, the metal−chloride bonds in both species are shorter than the values observed in similar chloride-bridged complexes such as $[Me_3AlClAlMe_3]^-$ (Al−Cl av 2.363 Å)[25] and $[(MeC)_4NMe_2AlClAlMe_2N(CMe)_4]^{1-}$ (Al−Cl av 2.335 Å).[26]

In the solid state, the Al−Cl−Al unit extends out over one side of the anthracene and dibenzofuran rings in **11** and **12**, inducing asymmetry between the two arms in the 2,2′-methylenebis(4,6-di-*tert*-butylphenoxide) groups. In solution, either the structure is symmetric or the position of the chloride atom equilibrates rapidly between both sides of the spacers. Variable-temperature ^1H NMR studies of **11** indicate that all four phenoxide groups are equivalent over a wide temperature range (−80 to +80 °C). The low-temperature ^1H NMR spectrum (−80 °C) of **11** showed relatively little effect in the overall symmetry of the binuclear structure and only a slight broadening of the $Al(CH_3)$ resonance. We attribute this observation to the increased contribution of the Al quadrupole at low temperatures and not rapid exchange of the chloride ion between the two metal centers. Demonstrating the robustness of these chloride bridges, no degradation of **11** or **12** was apparent with either the addition of excess NEt_4Cl or prolonged heating of the complex at 80 °C. To further demonstrate the stability of the Al−Cl−Al interaction, the ^{27}Al NMR was measured over a similar temperature range (−80 to 80 °C) for **11**, and only one resonance was observed (δ 60, $\omega_{1/2} = 4100$, RT), consistent with a four-coordinate aluminum center with two aryloxide donors.[27,28]

In contrast to **11** and **12**, the analogous reaction of NEt_4Cl with **8** afforded a different type of anionic complex, **13** (Scheme 7, Figure 9, Tables 4 and 5). The ^1H NMR spectrum of the reaction mixture indicated that there were several chemically inequivalent methyl groups. An asymmetric, dianionic, bimetallic aluminum complex was isolated in high yield from the reaction mixture, and in this molecule, one aluminum center binds two chloride anions while the other metal binds three of the four phenoxide groups from the ligand. Perhaps, some combination of the short distance between the two sets of 2,2′-methylenebis(4,6-di-*tert*-butylphenoxide) groups and the flexibility of the xanthene backbone induces an asymmetric cleavage of the Al_2O_2 unit in **8**. The isolation and characterization of **13** further highlights the divergent reactivity brought about by the different spacers integrated into the tetraphenoxide ligands. Alterations in the spacer can

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[25] Addition of potassium chloride to a solution of $AlMe_3$ and dibenzo-18-crown-6 affords $[Me_3AlClAlMe_3]^-$. Atwood, J. L.; Hrncir, D. C.; Rogers, R. D. *J. Inclusion Phenom.* **1983**, *1*, 199−207.

[26] The bridging chloride ligand in $[(MeC)_4NMe_2AlClAlMe_2N(CMe)_2]^-$ originates from the starting material, Me_2AlCl. Hausen, H. D.; Tödtmann, J.; Weidlein, J. *J. Organomet. Chem.* **1994**, *466*, C1−C4.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Bimetallic Compounds 8, 9, and 10

	8		**9**		**10**	
		X		X		X
			Bond Lengths (endocyclic distances)			
Al(1)−X	1.867(3)	O(1)	1.883(3)	O(1)	2.058(6)	C(71)
Al(1)−O(3)	1.848(3)		1.857(3)		1.806(3)	
Al(2)−X	1.834(3)	O(1)	1.862(3)	O(1)	2.109(6)	C(71)
Al(2)−O(3)	1.862(3)		1.879(3)		1.864(3)	
Al(1)···Al(2)	2.8079(19)		2.834(2)		2.671(2)	
			Bond Lengths (exocyclic distances)			
Al(1)−X	1.693(3)	O(2)	1.720(4)	O(2)	1.706(3)	O(1)
Al(2)−O(4)	1.751(3)		1.739(4)		1.696(4)	
Al(1)−X	1.923(5)	C(75)	1.950(5)	C(74)	1.700(3)	O(2)
Al(2)−X	1.931(5)	C(74)	1.942(5)	C(73)	1.912(5)	C(72)
Al(2)−C(61)	2.453(5)					
			Bond Angles (endocyclic angles)			
X−Al(1)−O(3)	81.15(13)	O(1)	81.48(14)	O(1)	93.37(19)	C(71)
X−Al(2)−O(3)	81.64(13)	O(1)	81.46(14)	O(1)	90.07(19)	C(71)
Al(1)−X−Al(2)	98.71(14)	O(1)	98.36(15)	O(1)	79.7(2)	C(71)
Al(1)−O(3)−Al(2)	98.41(13)		98.64(15)		93.38(14)	
			Bond Angles (exocyclic angles)			
O(1)−Al(1)−O(2)	115.44(15)		118.23(16)		120.13(15)	
O(2)−Al(1)−O(3)	104.93(15)		101.40(16)		116.12(16)	
O(1)−Al(1)−X	112.59(18)	C(75)	106.5(2)	C(74)	105.8(2)	C(71)
O(2)−Al(1)−X	114.6(2)	C(75)	116.8(2)	C(74)	103.4(2)	C(71)
O(3)−Al(1)−X	124.02(19)	C(75)	128.5(2)	C(74)	112.94(15)	O(1)
X−Al(2)−O(4)	103.14(14)	O(1)	105.43(16)	O(1)	121.1(2)	C(72)
O(3)−Al(2)−O(4)	118.18(14)		118.19(16)		106.55(16)	
X−Al(2)−X′	123.65(19)	O(1);C(74)	127.3(2)	O(1);C(73)	110.8(3)	C(71);C(72)
O(3)−Al(2)−X	108.20(18)	C(74)	106.4(2)	C(73)	118.2(2)	C(72)

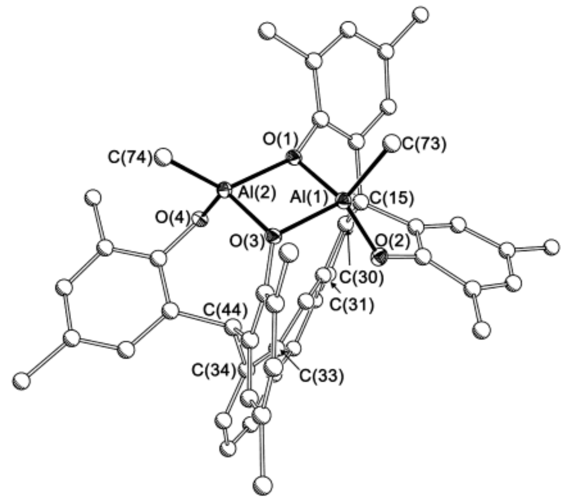

Figure 6. Diagram of the structure of **9** (30% probability ellipsoids for aluminum and oxygen atoms; carbon atoms drawn with arbitrary radii) highlighting the flexing of the anthracene backbone. Bonds to the aluminum atoms are indicated with solid lines. The *tert*-butyl methyl groups and all hydrogen atoms have been omitted for clarity.

both alter the distance between the two metal centers and modify the flexibility of the 2,2′-methylenebis(4,6-di-*tert*-butylphenoxide) arms, and as witnessed by the isolation of **6**−**13**, these changes have a profound impact on the reactivity of the different ligands.

If complexes **8**−**10** are to have utility for the activation of carbonyl groups, the bimetallic complexes need to be capable of accommodating Lewis basic substrates much larger than chloride. Accordingly, sodium phenoxide was added to solutions of **9**, and the solid-state structure revealed the product of the reaction, **14**, to be a bimetallic complex wherein a phenoxide anion has disrupted the Al_2O_2 interaction and inserted between the metal centers (Scheme 8, Figure 10, Table 4). Unlike the large and bulky tetraethylammonium cations in examples **11**−**13**, the sodium coordinates two opposing phenoxide groups from the ligands, forming a rare heterocyclic six-membered MAl_2O_3 (M = group 1) bridge.[29−31] In addition to ligating the two phenoxide oxygen atoms, the sodium binds an ether molecule (2.222(2) Å, Na(1)−O(6)). The metal−oxygen distances to the bridging phenoxide (av 1.863(2) Å) are slightly elongated relative to the ligand−metal distances (av 1.787(2) Å), but they are nearly indistinguishable from

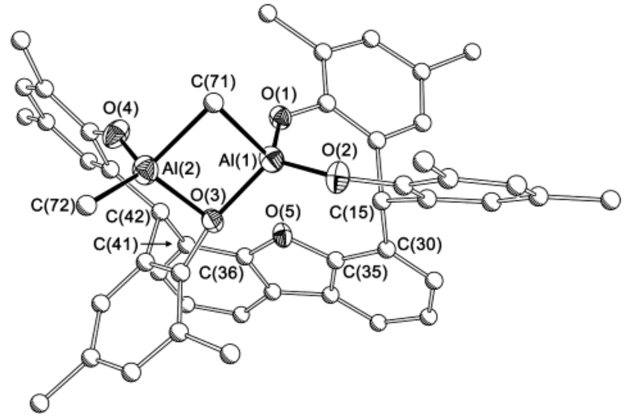

Figure 7. Diagram of the structure of **10** (30% probability ellipsoids for aluminum and oxygen atoms; carbon atoms drawn with arbitrary radii). Bonds to the aluminum atoms are indicated with solid lines. The *tert*-butyl methyl groups and all hydrogen atoms have been omitted for clarity.

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(27) Although ^{27}Al NMR data are in agreement with this formulation, the chemical shifts of aluminum species are highly dependent on the electronic environment *as well as* the coordination number. Barron, A. R. *Polyhedron* **1995**, *14*, 3197−3207.

(28) Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufińska, A.; Angermund, K.; Betz, P.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1991**, *411*, 37−55.

Table 4. X-ray Structural Data[a] for Compounds 12−17 and 19

	12·$1^1/_8$CH$_2$Cl$_2$	**13**·CH$_2$Cl$_2$·$^1/_4$C$_7$H$_8$	**14**·2CH$_2$Cl$_2$	**15**·C$_5$H$_{12}$	**16**·$2^1/_2$CH$_2$Cl$_2$	**17**·2CH$_2$Cl$_2$	**19**·4CH$_2$Cl$_2$
total no. of reflns	72 704	45 097	50 022	31 360	20 481	22 602	22 522
no. of unique reflns	11 586	26 207	15 819	11 338	11 098	14 925	13 660
R(int)	0.0943	0.0582	0.0647	0.0550	0.0578	0.0433	0.1508
θ_{max} (deg)	23.50	22.50	25.00	28.31	23.50	28.34	24.75
chem formula	$C_{81.125}H_{116.25}NO_5Al_2Cl_{3.25}$	$C_{93.75}H_{144}Al_2Cl_4N_2O_5$	$C_{86}H_{115}O_6Al_2Cl_4Na$	$C_{101}H_{136}O_6Al_2$	$C_{77.5}H_{100}O_6AlCl_5$	$C_{65}H_{83}O_6Al_3Cl_4$	$C_{81}H_{102}O_5Al_2Cl_8$
fw	1350.24	1574.87	1463.53	1500.06	1331.81	1183.05	1493.19
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	*Pbca*	$P\bar{1}$	*C*2/*c*	*P*2/*n*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
(Mo *K*α) (mm^{-1})	0.192	0.181	0.202	0.082	0.290	0.278	0.351
a (Å)	25.8599(15)	15.4309(7)	61.323(4)	16.6001(12)	14.214(3)	13.0989(14)	14.723(3)
b (Å)	19.8675(12)	25.6420(13)	13.5423(8)	11.9328(9)	15.116(3)	13.2760(14)	15.462(3)
c (Å)	30.5878(18)	28.1895(14)	21.6684(11)	24.8710(18)	20.095(4)	18.315(2)	19.938(4)
α (deg)		112.472(1)			104.122(5)	95.047(2)	69.973(4)
β (deg)		102.008(1)	93.043(1)	109.180(2)	106.091(4)	91.299(2)	72.995(4)
γ (deg)		90.449(1)			105.057(4)	94.424(2)	74.811(4)
V_c (Å^3)	15715.1(16)	10034.3(8	17969.3(17)	4653.1(6)	3766.5(13)	3161.9(6)	4011.3(12)
Z	8	4	8	2	2	2	2
R_1 [$I \geq 2\sigma(I)$][b]	0.0849 [8757]	0.0887 [14595]	0.0596 [10021]	0.0586 [7689]	0.0929 [6166]	0.0535 [9964]	0.0697 [3091]
wR_2 (all data)[c]	0.2043	0.2770	0.1706	0.1687	0.2981	0.1538	0.1656
diff peak, hole (e Å^{-3})	0.476, −0.459	1.066, −0.555	0.761, −0.286	0.364, −0.378	0.862, −0.544	0.524, −0.633	0.614, −0.519

[a] Obtained with monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) at 173 K. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

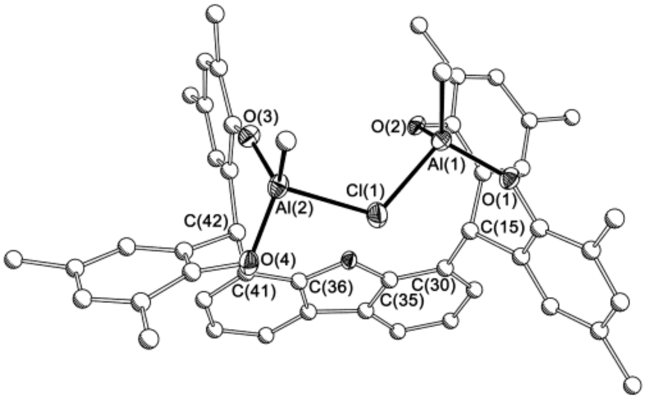
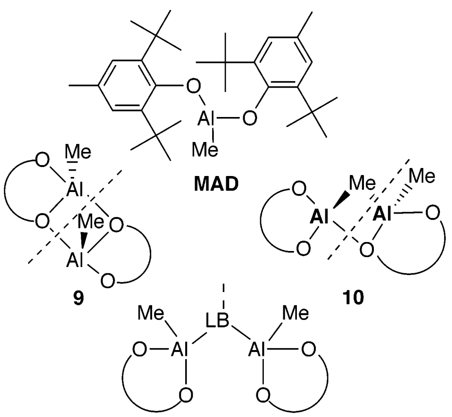
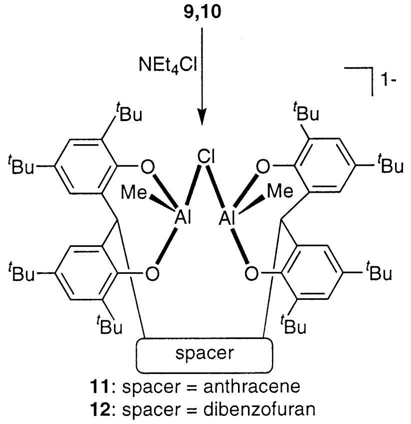


Figure 8. Diagram of the structure of **12** (30% probability ellipsoids for aluminum and oxygen atoms; carbon atoms drawn with arbitrary radii). Bonds to the aluminum atoms are indicated with solid lines. The *tert*-butyl methyl groups, the cation, and all hydrogen atoms molecules have been omitted for clarity.

Scheme 5



Scheme 6



the analogous bonds in [Li(CH$_2$NMe)$_3$](μ-OH)$_3$Al$_2${CH(SiMe$_3$)$_2$}$_4$ (1.897(3) Å), which incorporates a LiAl$_2$O$_3$ bridging unit.[29] The phenoxide anion is positioned on one side of the molecule to allow for the integration of the cation and to minimize steric interactions with the *tert*-butyl groups.

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(29) Uhl, W.; Hahn, I.; Koch, M.; Layh, M. *Inorg. Chim. Acta* **1996**, *249*, 33−39.

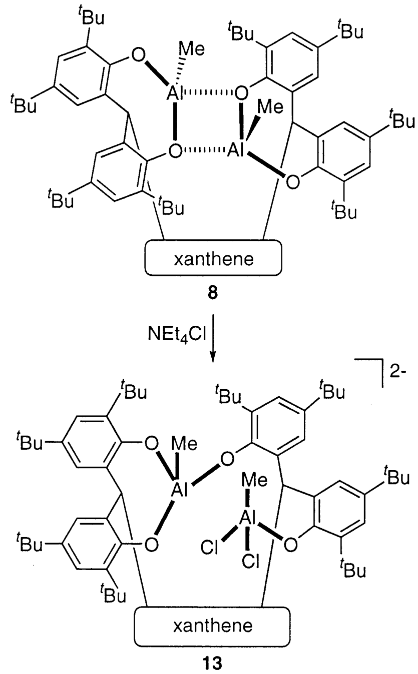
(30) Storre, J.; Schnitter, C.; Roesky, H. W.; Schmidt, H. G.; Noltmeyer, M.; Fleischer, R.; Stalke, D. *J. Am. Chem. Soc.* **1997**, *199*, 77505−7513.

(31) Nöth, H.; Schlegel, A.; Knizek, J.; Schwenk, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2640−2643.

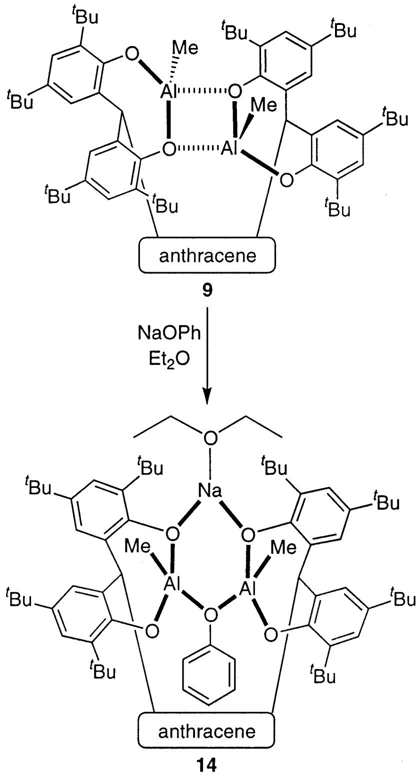
Table 5. Selected Bond Lengths (Å) and Angles (deg) for 11, 12, and 13

	11		12		13	
		X		X		X
			Bond Distances			
Al(1)−Cl(1)	2.3139(11)		2.2695(17)			
Al(2)−Cl(1)	2.3224(11)		2.3011(16)		2.201(3)	
Al(2)−Cl(2)	2.214(3)					
Al(1)−O(1)	1.762(2)		1.714(3)		1.773(4)	
Al(1)−O(2)	1.713(2)		1.737(3)		1.728(4)	
Al(1)−O(4)	1.743(4)					
Al(1)−X	1.932(3)	C(74)	1.946(4)	C(71)	2.012(5)	C(74)
Al(2)−O(3)	1.748(2)		1.711(3)		1.725(4)	
Al(2)−O(4)	1.708(2)		1.746(3)			
Al(2)−X	1.924(3)	C(73)	1.946(5)	C(72)	1.918(7)	C(75)
Al(1)−Al(2)	3.9886(12)		3.9186(18)		6.659(3)	
			Bond Angles			
Al(1)−Cl(1)−Al(2)	118.70(4)		118.04(7)			
O(1)−Al(1)−O(2)	112.05(10)		111.05(14)		108.98(19)	
O(1)−Al(1)−X	119.75(14)	C(74)	111.74(18)	C(71)	111.21(18)	O(4)
O(2)−Al(1)−X	111.40(13)	C(74)	118.54(19)	C(71)	105.2(2)	C(74)
O(1)−Al(1)−Cl(1)	105.70(7)		101.39(11)			
O(2)−Al(1)−Cl(1)	98.69(7)		105.32(11)			
Cl(1)−Al(1)−X	106.72(11)	C(74)	107.05(16)	C(71)		
O(3)−Al(2)−O(4)	114.55(10)		115.24(14)			
O(3)−Al(2)−X	119.54(13)	C(73)	108.8(2)	C(72)	111.21(18)	C(75)
O(4)−Al(2)−X	111.18(13)	C(73)	120.6(2)	C(72)		
O(3)−Al(2)−Cl(1)	98.77(8)		109.94(11)		108.92(16)	
O(4)−Al(2)−Cl(1)	105.39(8)		93.70(10)			
Cl(1)−Al(2)−X	105.00(11)	C(73)	106.79(16)	C(72)	102.33(12)	Cl(2)

Scheme 7



Scheme 8



Reactions of Bimetallic Species with Carbonyl Groups. In view of the promising reactivity observed upon the addition of hard Lewis bases, complexes **9** and **10** were both treated with simple ketones to test the viability of the species as bimetallic Lewis acid catalysts for organic transformations. Upon addition of a single equivalent of α,α,α-trimethylacetophenone to a solution of **9**, an immediate color change from pale yellow to red occurs. The ^{1}H NMR spectrum of the reaction mixture indicated a new species had indeed formed, but only half of the starting material had reacted. Subsequently, the reaction was repeated with 2 equiv of ketone, and in the ^{1}H NMR spectrum of solution, the resonance arising from one of the protons on the central anthracene ring shifted upfield from δ 11.15 ppm in **9** to δ 8.22 ppm. This upfield shift suggested that the bridging interaction directly above the anthracene linker had been disrupted. After several days at −35 °C, large single crystals of **15** were obtained directly from the reaction mixture in moderate yield, and as illustrated in Figure 11 (Tables 4 and 7), the addition of ketone to **9** had indeed split apart the Al_2O_2 structure. To bind 2 equiv of α,α,α-trimethylacetophenone, the aluminum has inverted the orientation of the phenoxide arms in the

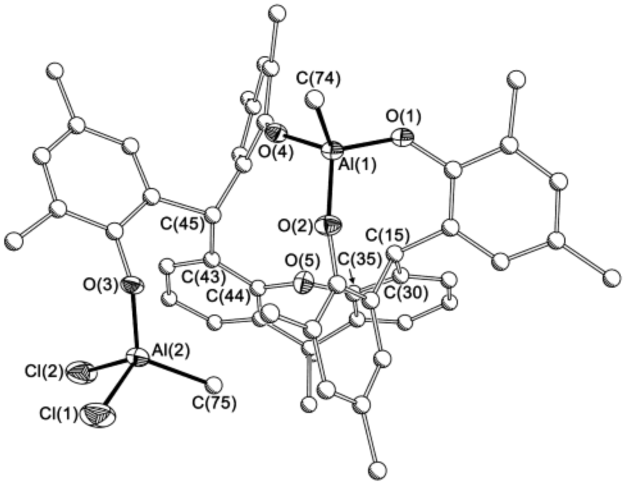


Figure 9. Diagram of one of the two symmetry-independent anions of **13** in the solid-state structure of the compound (30% probability ellipsoids for aluminum and oxygen atoms; carbon atoms drawn with arbitrary radii). The second molecule maintains an identical structure. Bonds to the aluminum atoms are indicated with solid lines. The *tert*-butyl methyl groups, the cations, and all hydrogen atoms have been omitted for clarity.

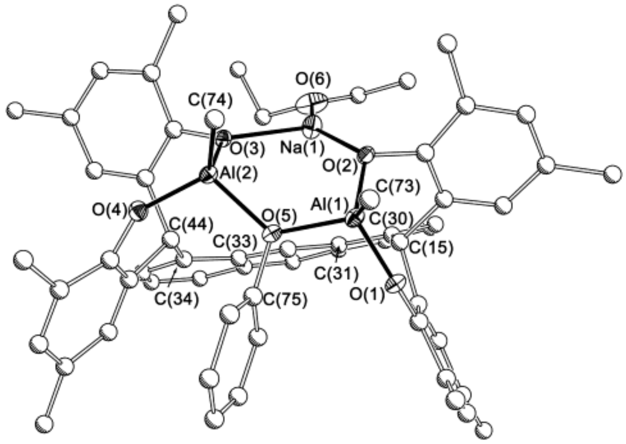


Figure 10. Diagram of the structure of **14** (30% probability ellipsoids for aluminum and oxygen atoms; carbon atoms drawn with arbitrary radii). Bonds to the aluminum atoms are indicated with solid lines. The *tert*-butyl methyl groups and all hydrogen atoms have been omitted for clarity.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Phenoxide-Bridged Compound 14

Bond Distances	
Na(1)−O(6)	2.222(2)
Na(1)−O(3)	2.255(2)
Na(1)−O(2)	2.2939(18)
Al(1)−O(1)	1.7151(16)
Al(1)−O(2)	1.7974(17)
Al(1)−O(5)	1.8572(18)
Al(1)−C(73)	1.941(3)
Al(2)−O(4)	1.7091(18)
Al(2)−O(3)	1.7751(17)
Al(2)−O(5)	1.8691(17)
Al(2)−C(74)	1.942(3)
Bond Angles	
O(2)−Na(1)−O(3)	93.93(7)
O(2)−Al(1)−O(5)	98.24(8)
O(3)−Al(2)−O(5)	103.68(8)
Al(1)−O(2)−Na(1)	131.44(9)
Al(2)−O(3)−Na(1)	123.93(8)
Al(1)−O(5)−Al(2)	125.08(9)

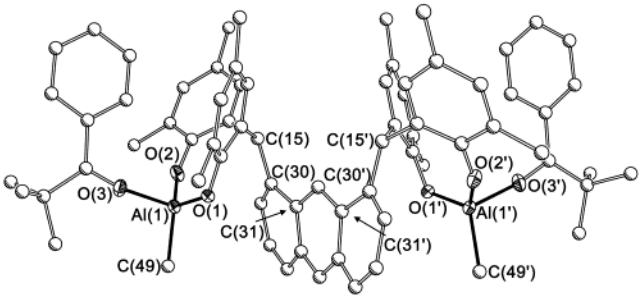


Figure 11. Diagram of the structure of **15** (30% probability ellipsoids for aluminum and oxygen atoms; carbon atoms drawn with arbitrary radii) highlighting the flexing of the anthracene backbone. Primed and unprimed atoms are related by a C_2-symmetry operation. Bonds to the aluminum atoms are indicated with solid lines. The *tert*-butyl methyl groups and all hydrogen atoms have been omitted for clarity.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for Compounds 15 and 16

15		16	
Bond Lengths			
Al(1)−O(1)	1.7134(14)	Al(1)−O(1)	1.719(4)
Al(1)−O(2)	1.7247(13)	Al(1)−O(2)	1.711(3)
Al(1)−O(3)	1.8924(13)	Al(1)−O(3)	1.682(3)
Al(1)−C(49)	1.938(2)	Al(1)−O(6)	1.878(4)
O(3)−C(38)	1.238(2)	O(6)−C(71)	1.238(6)
Bond Angles			
O(1)−Al(1)−O(2)	117.24(6)	O(1)−Al(1)−O(2)	118.52(17)
O(1)−Al(1)−O(3)	97.58(6)	O(1)−Al(1)−O(2)	118.52(17)
O(2)−Al(1)−O(3)	101.29(6)	O(1)−Al(1)−O(6)	98.20(17)
O(1)−Al(1)−C(49)	116.58(9)	O(2)−Al(1)−O(3)	115.75(18)
O(2)−Al(1)−C(49)	114.13(9)	O(2)−Al(1)−O(6)	100.89(18)
O(3)−Al(1)−C(49)	106.36(8)	O(3)−Al(1)−O(6)	102.54(17)

2,2′-methylenebis(4,6-di-*tert*-butylphenoxide) groups with respect to the central methine hydrogen atom (Scheme 9). With the reorientation of the phenolic arms, all four bulky *para*-*tert*-butyl groups are forced in the same location over the anthracene spacer, inducing a twist of 32.5° in the planes defined by C(15),C(30),C(31) and C(15′),C(30′),C(31′). All other aspects of the structure are unexceptional. The split, inverted structure appears to be quite common when neutral Lewis bases are added, and compounds analogous to **15** were isolated upon addition of Et_2O, THF, cyclopentanone, cyclohexanone, acetophenone, benzaldehyde, DMF, or tetramethyl thiourea to solutions containing **9**.[32]

With the rigid dibenzofuran backbone, reactions of **10** with small ketone substrates (i.e., cyclopentanone and cyclohexanone) afforded entirely different complexes (Scheme 10). For instance, when cyclopentanone was added to a stirred solution of **10** in pentane, a precipitate formed after several minutes. The ^1H NMR spectrum of the product, **16**, indicated that all of the aluminum alkyls had been lost and a resonance associated with a phenolic proton was clearly evident. The resonance at δ 240.2 ppm in the ^{13}C NMR spectrum of **16** also indicated the cyclopentanone carbonyl was deshielded relative to neat cyclopentanone (δ 209.6 ppm) as well as the complex formed upon addition of cyclopentanone to MAD (δ 232.8 ppm).[33] In the solid-state structure of

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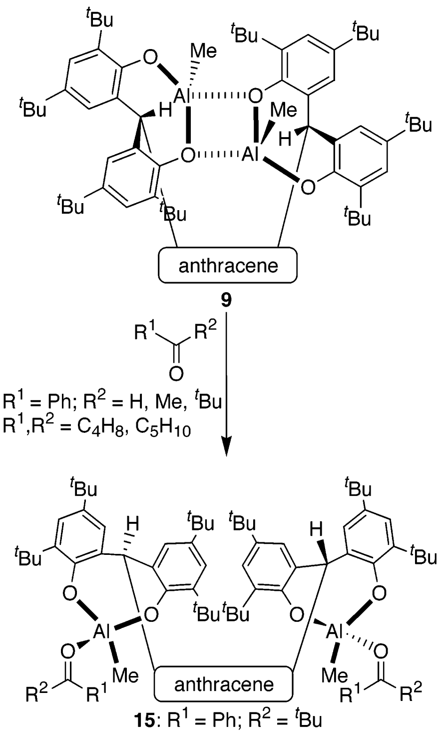
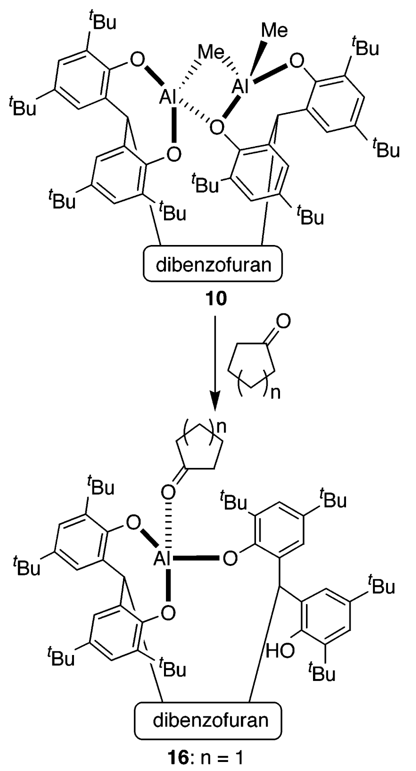
(32) Cottone, A.; Scott, M. J. Unpublished results.

Scheme 9



Scheme 10



16 depicted in Figure 12 (Tables 4 and 7), a single aluminum center is bound by three of the four phenolic arms from the ligand, and the fourth arm has been protonated, possibly due to the presence of trace water in the reaction mixture. Completing the tetrahedral coordination sphere, a cyclopentanone oxygen is bound at a distance of 1.878(4) Å from the aluminum center.

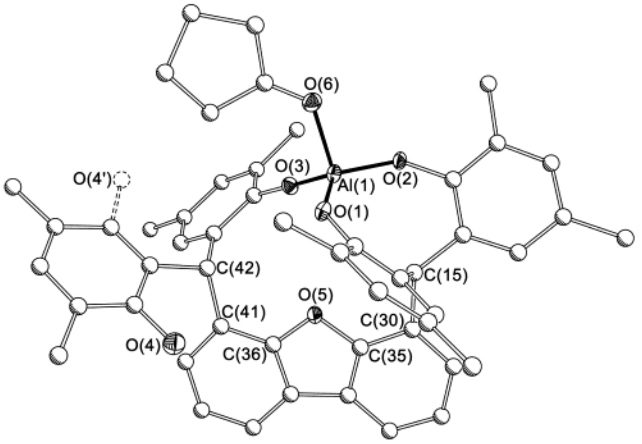


Figure 12. Diagram of the structure of **16** (30% probability ellipsoids for aluminum and oxygen atoms; carbon atoms drawn with arbitrary radii). Bonds to the aluminum atoms are indicated with solid lines. The *tert*-butyl methyl groups and all hydrogen atoms have been omitted for clarity. The phenolic arm bearing O(4) was disordered across two positions, and the oxygen atom in the O(4′) position was modeled with a site occupancy of 15%.

One of the phenoxides in the ligand spans the length of the spacer and binds the aluminum with a short bond of 1.682(3) Å and a nearly linear C(44)−O(3)−Al(1) angle of 175.9(3)°. The bond distances from the aluminum to the other two phenoxide arms are somewhat longer (1.711(3) and 1.719(4) Å). The angles around the aluminum center are not significantly distorted from idealized tetrahedral geometry. Despite the addition of numerous substrates, complexes with the dibenzofuran linker never formed the "split" structure (such as **15**) commonly observed with the anthracene spacer, perhaps due to either the unusual Al−Me−Al−O unit in **10** or, more likely, the rigidity of the dibenzofuran spacer in comparison to the anthracene linker.

Decreasing the Steric Constraints in the Bifunctional Lewis Acids. The inversion of the arms with respect to the central methine witnessed in **15** as well as the isolation of the mononuclear complex **16** may be due in part to the obstruction of the reactive aluminum center by the *tert*-butyl groups on the *ortho*-position of the phenoxide donors. Hence, the ligand 4,4′,4″,4‴-tetra-*tert*-butyl-6,6′,6″,6‴-tetramethyl-2,2′,2″,2‴-(4,6-dibenzofuranmethanediyl)tetraphenol, **4**H_4, was prepared in order to alleviate steric clash by placing methyls rather than *tert*-butyl groups at the *ortho*-position of the phenoxides. Regardless of stoichiometry used, the reaction between **4**H_4 and trimethylaluminum produced a single product. The ^{1}H and ^{13}C NMR spectra of this material exhibited four inequivalent *tert*-butyl resonances and five Al-Me signals. The trimetallic product, **17**, was isolated as a crystalline product, and the structure is depicted in Figure 13 and Scheme 11. Crystallogrphic data can be found in Tables 3 and 8. The compound contains a cyclic Al_3O_3 ring in a distorted chair conformation with three of the four phenoxide donors bridging between the aluminum centers. All three metals are tetrahedral; two aluminums are bound by two methyl ligands and two phenoxides, while the third contains one methyl group and three phenoxides. The six endocyclic Al−O bonds vary slightly from 1.8340(14) Å to 1.8765(14) Å, except for Al(3)−O(4),

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(33) Power, M. B.; Bott, S. G.; Atwood, J. L.; Barron, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 3446−3451.

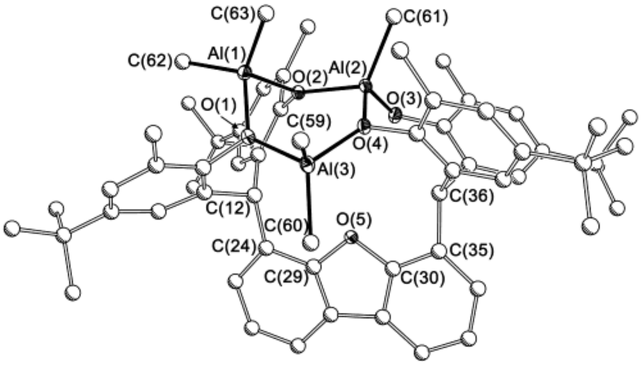
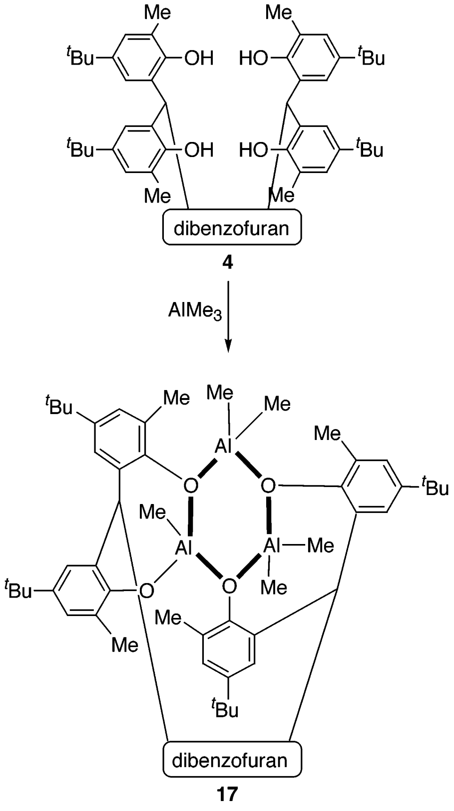


Figure 13. Diagram of the structure of **17** (30% probability ellipsoids for aluminum and oxygen atoms; carbon atoms drawn with arbitrary radii). Bonds to the aluminum atoms are indicated with solid lines. All hydrogen atoms have been omitted for clarity.

Scheme 11



which has a bond length of 1.9362(15) Å. The aluminum−carbon bond lengths and angles are unremarkable. The lone exocylcic aluminum−phenoxide bond, Al(2)−O(3), is significantly shorter (1.7276(15) Å) than the endocyclic counterparts. The O−Al−O angles incorporated in the six-membered ring range from 91.86(6)° to 99.44(6)°, while the corresponding Al−O−Al angles vary from 118.37(7)° to 134.64(7)°. Compounds incorporating Al_3O_3 units often form more complex interactions such as the fused cage systems found in $[(tert\text{-Bu})_6Al_6(\mu_3\text{-O})_4(\mu\text{-O})_2(NH_2Bu)_2]$,[34] but several discrete examples of six-membered Al_3O_3 ring systems exhibiting distorted boat conformations have been isolated. The structural parameters of these complexes are somewhat distinct from **17**.[35−37] For instance, the Al_3O_3 unit in $[(CH_3)_2AlON(CH_3)_2]_3$ contains similar Al−O distances of 1.849(1)−1.888(1) Å, but the O−Al−O angles of 89.43(5)−92.90(5)° are slightly more acute than **17** and the Al−O−Al angles of 132.62(5)−142.97(6)° are more obtuse.[36] In the C_3-symmetric complex [(tris(3,5-di-*tert*-butyl-2-phenoxy)methane)Al_3Me_6], the aluminum−oxygen distances in the Al_3O_3 core are marginally longer in comparison to **17**, ranging from 1.895(2) to 1.918(2) Å, while the average Al−O−Al angle of 124.3(2)° is similar.[37] Since it contains a trimetallic core, the reactivity of **17** with Lewis bases was not investigated.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for Trimetallic Compound 17

Bond Distances

Al(1)−O(1)	1.8611(15)	Al(2)−C(61)	1.938(2)
Al(1)−O(2)	1.8765(14)	Al(3)−O(1)	1.8721(15)
Al(1)−C(62)	1.944(2)	Al(3)−O(4)	1.9362(15)
Al(1)−C(63)	1.946(2)	Al(3)−C(59)	1.947(2)
Al(2)−O(2)	1.8340(14)	Al(3)−C(60)	1.941(2)
Al(2)−O(3)	1.7276(15)	Al(1)···Al(2)	3.1868(6)
Al(2)−O(4)	1.8662(15)	Al(1)···Al(3)	3.3416(9)
		Al(2)···Al(3)	3.5085(9)

Bond Angles

O(1)−Al(1)−O(2)	91.86(6)	Al(1)−O(1)−Al(3)	127.04(8)
O(2)−Al(2)−O(4)	98.90(6)	Al(2)−O(2)−Al(1)	118.37(7)
O(1)−Al(3)−O(4)	99.44(6)	Al(2)−O(4)−Al(3)	134.64(7)

Since methyl substitution at the *ortho*-position of the phenolic groups allows for the formation of trimetallic species, 4,4′,4″,4‴-tetra-*tert*-butyl-6,6′,6″,6‴-tetra-isopropyl-2,2′,2″,2‴-(1,8-anthracenemethanediyl)tetraphenol, **5**H_4, was prepared to probe the attributes of the isopropyl-substituted ligand system. Isopropyl groups were thought to be large enough to allow for the formation of a bifunctional Lewis acid complex, yet the coordination spheres of the metals should be more accessible in comparison to complexes with **2**. Addition of trimethylaluminum to a solution of **5**H_4 afforded a new species, and the ^{1}H NMR spectrum of the reaction mixture exhibited a lone resonance for the Al-CH_3 group and four inequivalent alkyl signals, similar to **8**, **9**, and **10**. Furthermore, the downfield shift of the significantly deshielded proton on the anthracene to δ 10.82 ppm indicated a bridged aluminum species had formed (Scheme 12). The NMR and analytical data were consistent with the formation of the bifunctional Al_2O_2-bridged species, **18**, analogous to **9**.

The addition of substrates containing carbonyl groups to solutions of **18** consistently disrupted the Al_2O_2 core, and the red product from the reaction between **18** and 1 equiv of benzaldehyde, **19**, was isolated as a crystalline material. The ^{1}H NMR spectrum of the reaction mixture suggested that the molecule did not contain an axis of symmetry, and the benzaldehyde phenyl resonances were shifted upfield. The complex was characterized by X-ray crystallography, and as depicted in Figure 14 (Tables 4 and 9), the solid-state structure is consistent with the NMR data. Rather than inverting the orientation of the arms with respect to the hydrogen on the linking carbon as in **15** or bridging between the metals

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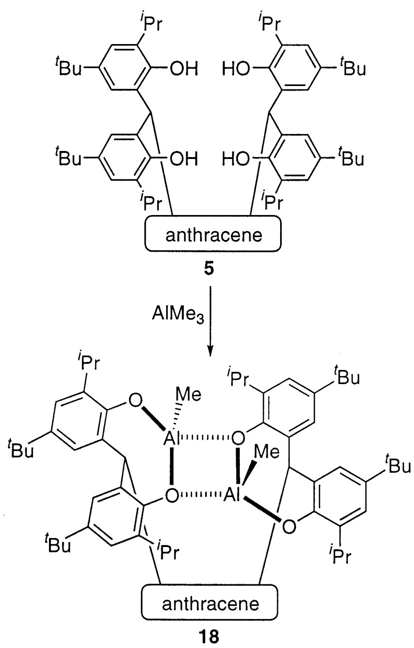
[34] Koide, Y.; Bott, S G.; Barron, A. R. *Organometallics* **1996**, *15*, 5514−5518.

[35] Gelbrich, T.; Dümichen, U.; Jörchel, P. *Acta Crystallogr., Sect. C* **1999**, *55*, 856−858.

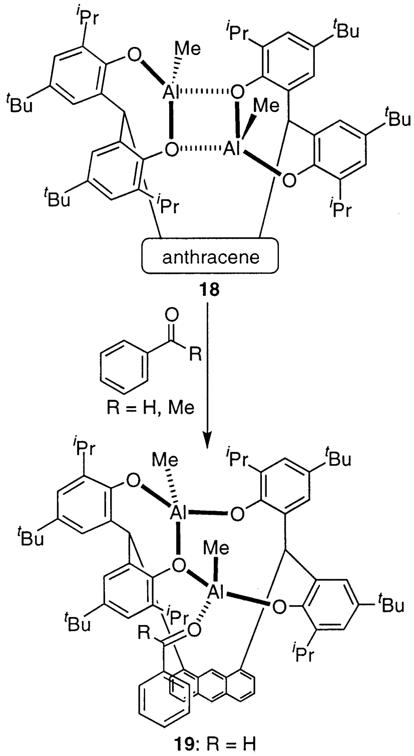
[36] Hausen, H. D.; Schmoger, G.; Schwarz, W. J. *Organometallics* **1978**, *153*, 271−279.

[37] Cottone, A., III; Morales, D.; Lecuivre, J. L.; Scott, M. J. *Organometallics* **2002**, *21*, 418−428.

Scheme 12



Scheme 13



19: R = H

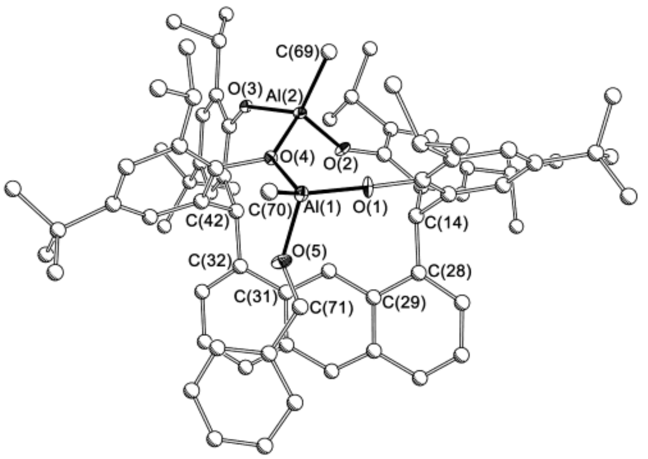


Figure 14. Diagram of the structure of **19** (30% probability ellipsoids for aluminum and oxygen atoms; carbon atoms drawn with arbitrary radii). Bonds to the aluminum atoms are indicated with solid lines. All hydrogen atoms have been omitted for clarity.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for Compound 19

	Bond Distances		
Al(1)−O(1)	1.666(5)	Al(2)−O(2)	1.728(5)
Al(1)−O(4)	1.820(4)	Al(2)−O(3)	1.737(4)
Al(1)−O(5)	1.843(6)	Al(2)−O(4)	1.892(5)
Al(1)−C(70)	1.933(6)	Al(2)−C(69)	1.938(7)
O(5)−C(71))	1.219(9)	Al(1)···Al(2)	3.377(3)
	Bond Angles		
O(1)−Al(1)−O(4)	107.5(2)	O(2)−Al(2)−O(3)	109.5(2)
O(1)−Al(1)−O(5)	109.2(3)	O(2)−Al(2)−O(4)	105.5(2)
O(4)−Al(1)−O(5)	97.5(2)	O(3)−Al(2)−O(4)	96.7(2)
O(1)−Al(1)−C(70)	118.1(3)	O(2)−Al(2)−C(69)	115.0(3)
O(4)−Al(1)−C(70)	120.9(3)	O(3)−Al(2)−C(69)	119.0(3)
O(5)−Al(1)−C(70)	100.7(3)	O(4)−Al(2)−C(69)	108.8(3)

as in **11**, the benzaldehyde group is bound to a single aluminum center at a distance of 1.843(6) Å. In addition to the aldehyde oxygen, the coordination sphere of Al(1) contains one alkyl group, as well as one bridging and one terminal phenoxide group from opposite 2,2′-methylenebis(4,6-di-*tert*-butylphenoxide) arms (Scheme 13). The second aluminum center also adopts a tetrahedral geometry with three phenoxide ligands and one alkyl group. Perhaps demonstrating the stability of this complex, the two planes of the anthracene defined by C(14),C(28),C(29) and C(42),C(32),C(31) are only distorted by 7.5°. Interestingly, the proximity of the benzaldehyde phenyl group to the anthracene ring (~3.2 Å) induces the upfield shift of the benzaldehyde protons witnessed in the ^{1}H NMR spectrum. Addition of similar substrates, such as acetophenone, to solutions of **18** formed compounds analogous to **19**, and the reactivity of **18** was not explored further.[32]

Conclusions

Recent developments with designer Lewis acids such as MAD have highlighted the utility of these bulky complexes in various areas of chemistry. As an extension of this work, we have synthesized several tetraphenoxide ligands to provide a rigid ligand framework capable of holding two aluminum species akin to MAD in close proximity. The reaction of trimethylaluminum with the ligands proves to be a suitable pathway for the preparation of bifunctional Lewis acidic assemblies, and due to the unique ability to substitute different flexible and rigid aromatic linkers into the ligand backbone, divergent bimetallic complexes can be isolated. Solid-state studies have illustrated that these bifunctional complexes incorporate a stabilizing four-membered Al_2O_2 or Al_2MeO core structure with at least one phenoxide group spanning the metal centers. The formation of these intramolecular bridges, however, does not hinder the reactivity of the complexes. Both **9** and **10** rapidly react with Lewis bases such as chloride and phenoxide, and the resulting species are rare examples of well-defined compounds wherein both metals simultaneously coordinate to a single external Lewis base. In contrast to the symmetrical bidentate interaction with anions, the analogous reaction with carbonyl substituents affords either C_2-symmetric binuclear species with two bound substrates or an unusual mononuclear complex with the carbonyls exclusively binding in a η^1-mode, possibly due to the steric bulk of *tert*-butyl groups *ortho* to the phenoxide donor. Fortunately, the synthetic methodology utilized for the ligand is extremely general, and as demonstrated above, the ligand attributes such as the flexibility and size of the spacer as well as the steric constraints of the phenol arms have a profound effect on the reactivity of the ligand and the resulting complexes. Along with efforts to further refine the ligand system to induce cooperative binding of carbonyl groups in the bimetallic species, investigations into the utility of the complexes outlined above for the catalysis of organic transformations are currently underway.

Experimental Section

Unless noted otherwise, all manipulations were carried out under an inert atmosphere of N_2 in a drybox or on a vacuum line using standard techniques. All solvents were dried and distilled prior to use. NMR spectra were recorded at room temperature on a Mercury 300 MHz spectrometer at 299.95 and 75.47 MHz for the proton and carbon channels, respectively. ^{27}Al NMR spectra were recorded on a 300 MHz VXR spectrometer at 78.16 MHz. The University of Florida Spectroscopic Services performed elemental analyses for compounds **1**H_4−**5**H_4, while Atlantic Microlabs analyzed the air-sensitive complexes. In the solid state, the aluminum complexes all crystallized with solvent molecules, and despite attempts to gently remove the solvent under vacuum, the elemental analysis data and ^{1}H NMR data indicated residual solvate molecules remained in the bulk material in most instances. The residual solvate molecules were included in the molecular weight of the compounds for the calculation of the yields. Melting points were determined using a capillary melting point apparatus and are uncorrected.

Preparation of 4,4′,4″,4‴-Tetra-*tert*-butyl-6,6′,6″,6‴-tetra-*tert*-butyl-2,2′,2″,2‴-(1,8-anthracenemethanediyl)tetraphenol (1H$_4$). A 1.00 g (4.27 mmol) portion of 1,8-anthracene dicarboxaldehyde[38] was added to 2,4-di-*tert*-butylphenol (22.0 g, 107 mmol). The mixture was heated to 96 °C, and after stirring for 1 h, the homogeneous solution was deep red. An aliquot of concentrated HCl (1.5 mL) was added to the solution, and the mixture was stirred for 12 h. The purple solution was allowed to cool and stirred in a mixture of CH_3CN (40 mL) and water (10 mL) overnight. The product was isolated, washed with CH_3CN, and dried to yield 3.64 g of a gray solid (82%), mp 194 °C (dec). Anal. Calcd for $C_{72}H_{94}O_4$: C, 84.48; H, 9.26. Found: C, 83.82; H, 9.54. ^{1}H NMR ($CDCl_3$): δ 8.85 (s, anthracene-H, 1H), 8.48 (s, anthracene-H, 1H), 7.93 (d, anthracene-H, J = 8.5 Hz, 2H), 7.36 (dd, anthracene-H, J = 7.1, 8.5 Hz, 2H), 7.21 (d, aryl-H, J = 2.3 Hz, 4H), 7.04 (d, anthracene-H, J = 7.1 Hz, 2H), 6.66 (d, aryl-H, J = 2.3 Hz, 4H), 6.29 (s, CH, 2H), 4.77 (br s, OH, 4H), 1.38 (s, *t*-Bu, 36H), 1.05 (s, *t*-Bu, 36H). ^{13}C NMR ($CDCl_3$): δ 150.0, 142.1, 137.6, 136.1, 131.7, 130.0, 127.9, 127.7, 127.4, 126.0, 125.3, 125.0, 122.5, 120.2, 41.0, 34.9, 34.3, 31.5, 30.1. High-resolution FAB-MS: calcd 1022.715 (M$^+$), found 1022.720.

Preparation of 4,4′,4″,4‴-Tetra-*tert*-butyl-6,6′,6″,6‴-tetra-*tert*-butyl-2,2′,2″,2‴-(4,6-dibenzofuranmethanediyl)tetraphenol (2H$_4$). The condensation of 2,4-di-*tert*-butylphenol (9.20 g, 44.7 mmol) and 4,6-dibenzofurandicarboxaldehyde[39] (0.50 mg, 2.23 mmol) was carried out in a manner similar to **1**H_4. The product was isolated, washed, and dried to yield 1.92 g (85%) of a light pink solid, mp 139−141 °C. Anal. Calcd for $C_{70}H_{92}O_5$: C, 82.95; H, 9.16. Found: C, 82.48; H, 9.24. ^{1}H NMR ($CDCl_3$): δ 8.00 (d, dibenzofuran-H, J = 7.7 Hz, 2H), 7.32 (dd, dibenzofuran-H, J = 7.3, 7.7 Hz, 2H), 7.24 (d, aryl-H, J = 2.3 Hz, 4H), 7.13 (d, dibenzofuran-H, J = 7.3 Hz, 2H), 6.81 (d, aryl-H, J = 2.3 Hz, 4H), 6.12 (s, CH, 2H), 4.78 (bs, OH, 4H), 1.36 (s, *t*-Bu, 36H), 1.13 (s, *t*-Bu, 36H). ^{13}C NMR ($CDCl_3$): 154.3, 150.8, 142.7, 136.8, 127.7, 126.4, 125.6, 124.7, 124.4, 123.6, 123.3, 119.9, 40.7, 35.2, 34.5, 31.7, 30.1. High-resolution FAB-MS: calcd 1013.702 (M$^+$), found 1013.705.

Preparation of 4,4′,4″,4‴-Tetra-*tert*-butyl-6,6′,6″,6‴-tetra-*tert*-butyl-2,2′,2″,2‴-(4,5-methanediyl-9,9-dimethylxanthenel)tetraphenol (3H$_4$). 2,4-Di-*tert*-butylphenol (15.5 g, 75.2 mmol) and 4,5-diformyl-9,9-dimethylxanthene[40] (1.00 g, 3.76 mmol) were reacted in a procedure similar to **1**H_4. The product was filtered, washed with CH_3CN, and dried to yield 3.61 g of a white solid (91%), mp 252 °C (dec). Anal. Calcd for $C_{73}H_{98}O_5$: C, 83.06; H, 9.36. Found: C, 83.58; H, 9.50. ^{1}H NMR ($CDCl_3$): δ 7.39 (dd, xanthene-H, J = 7.9 Hz, 1.3 Hz, 4H), 7.23 (d, aryl-H, J = 2.3, 2H), 6.97 (t, xanthene-H, J = 7.7 Hz, 2H), 6.50 (dd, xanthene-H, J = 7.7 Hz, J = 1.2 Hz, 2H), 6.44 (d, aryl-H, J = 2.1 Hz, 4H), 5.30 (s, CH, 2H), 4.43 (s, OH, 4H), 1.69 (s, Me, 6H), 1.31 (s, *t*-Bu, 36H), 1.09 (s, *t*-Bu, 36H). ^{13}C NMR ($CDCl_3$): δ 150.8, 147.8, 145.5, 136.9, 129.7, 128.1, 128.0, 126.3, 125.5, 124.0, 123.4, 123.2, 41.3, 35.2, 34.5, 34.4, 33.2, 31.7, 30.0.

Preparation of 4,4′,4″,4‴-Tetra-*tert*-butyl-6,6′,6″,6‴-tetramethyl-2,2′,2″,2‴-(4,6-dibenzofuranmethanediyl)tetraphenol (4H$_4$). The condensation of 2-methyl-4-*tert*-butylphenol (7.32 g, 44.6 mmol) and 4,6-dibenzofurandicarboxaldehyde[39] (0.50 mg, 2.23 mmol) was adapted from the procedure utilized in **1**H_4. The product was collected, washed, and dried to yield 1.52 g (79%) of a white powder, mp 207 °C. Anal. Calcd for $C_{58}H_{68}O_5$: C, 82.41; H, 8.12. Found: C, 82.09; H, 7.94. ^{1}H NMR ($CDCl_3$): δ 7.85 (dd, dibenzofuran-H, J = 7.8 Hz, 0.9 Hz, 2H), 7.28 (t, dibenzofuran-H, J = 7.7 Hz, 2H), 7.15 (d, dibenzofuran-H, J = 6.9 Hz, 2H), 7.06 (d, aryl-H, J = 2.1 Hz, 4H), 6.94 (d, aryl-H, J = 2.4 Hz, 4H), 6.45 (s, CH, 2H), 5.00 (br, OH, 4H), 2.24 (s, Me, 9H), 1.14 (s, *t*-Bu, 36H). ^{13}C NMR ($CDCl_3$): 154.3, 149.8, 143.2, 128.2, 127.0, 126.6, 124.7, 124.5, 124.4, 124.0, 123.1, 119.5, 38.9, 34.2, 31.7, 16.7.

Preparation of 4,4′,4″,4‴-Tetra-*tert*-butyl-6,6′,6″,6‴-tetraisopropyl-2,2′,2″,2‴-(1,8-anthracenemethanediyl)tetraphenol (5H$_4$). The condensation of 2-isopropyl-4-*tert*-butylphenol (16.5 g, 85.9 mmol) and 1,8-anthracene dicarboxaldehyde[38] (1.00 g, 4.27 mmol) was carried out in a manner similar to **1**H_4. The product was isolated, washed with CH_3CN, and dried to yield 2.91 g of a white solid (83%). Crystals suitable for X-ray and elemental analysis were obtained from evaporation of an acetone solution, mp 173 °C (dec). Anal. Calcd for $C_{68}H_{86}O_4\cdot 1^1/_2C_3H_6O$: C, 82.59; H, 9.08. Found: C, 82.62; H, 9.10. ^{1}H NMR ($CDCl_3$): δ 8.80 (s, anthracene-H, 1H), 8.44 (s, anthracene-H, 1H), 7.90 (d, anthracene-H, J = 8.5 Hz, 2H), 7.35 (dd, anthracene-H, J = 6.9, 8.5 Hz, 2H), 7.13 (d, aryl-H, J = 2.3 Hz, 4H), 7.05 (d, anthracene-H, J = 6.6 Hz, 2H), 6.71 (d, aryl-H, J = 2.3 Hz, 4H), 6.34 (s, CH, 2H), 4.95 (s, OH, 4H), 3.22 (m, isopropyl-H, J = 6.9 Hz, 4H), 1.21 (d, isopropyl-CH_3, J = 6.8 Hz, 12H), 1.23 (d, isopropyl-CH_3, J = 6.8 Hz, 12H), 1.08 (s, *t*-Bu, 36H). ^{13}C NMR ($CDCl_3$): δ 150.0, 142.1, 137.6, 136.1, 131.7, 130.0, 127.9, 127.7, 127.4, 126.0, 125.3, 125.0, 122.5, 120.2, 41.0, 34.9, 34.3, 31.5, 30.1.

Synthesis of [(1)Al$_4$Me$_8$] (6). A 2.0 M solution of trimethylaluminum in hexanes (391 μL, 0.782 mmol) was added to **1**H_4 (200 mg, 0.196 mmol) in 25 mL of pentane at 0 °C. The solution was allowed to react for 1 h, and the solvent was removed. The residue was treated with 5 mL of CH_2Cl_2 and

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[38] Guilard, R.; Lopez, M. A.; Tabard, A.; Richard, P.; Lecomte, C.; Brandes, S.; Hutchison, J. E.; Collman, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 9877−9889.

[39] Skar, M. L.; Svendsen, J. S. *Tetrahedron* **1997**, *53*, 17425−17440.

cooled to −35 °C. Crystals formed after several days and were isolated to give a yield of 152 mg (62%). Following this methodology, the addition of 2 equiv of trimethylaluminum to **1**H_4 afforded only a mixture of **6** and unreacted **1**H_4. ^{1}H NMR (C_6D_6): δ 8.70 (s, anthracene-*H*, 1H), 8.29 (s, anthracene-*H*, 1H), 7.68 (d, anthracene-*H*, J = 8.3 Hz, 2H), 7.51 (d, anthracene-*H*, J = 7.3 Hz, 2H), 7.32 (d, aryl-*H*, J = 2.1 Hz, 2H), 7.22 (d, aryl-*H*, J = 1.9 Hz, 2H), 7.07 (dd, anthracene-*H*, J = 7.9 Hz, 7.5 Hz, 2H), 6.93 (d, aryl-*H*, J = 2.1 Hz, 2H), 6.83 (d, aryl-*H*, J = 1.9 Hz, 2H), 6.31 (s, C*H*, 2H), 1.42 (s, *t*-Bu, 18H), 1.41 (s, *t*-Bu, 18H), 1.16 (s, *t*-Bu, 18H), 1.08 (s, *t*-Bu, 18H), 0.37 (s, AlCH_3, 6H), −0.03 (s, AlCH_3, 6H), −0.17 (s, AlCH_3, 6H), −1.10 (s, AlCH_3, 6H). ^{13}C NMR (C_6D_6): δ 154.4, 147.3, 145.3, 141.1, 140.3, 138.8, 137.6, 135.9, 135.8, 133.1, 132.9, 132.1, 131.7, 131.4, 130.2, 124.6, 123.8, 122.7, 122.3, 119.6, 46.6, 35.7, 35.5, 34.8, 34.6, 32.3, 31.9, 31.7, 30.1, −3.9, −4.3, −8.2, −9.8. The compound is moderately temperature sensitive in the solid state and slowly decomposes to an unidentified species, hindering analysis of the material. Soon after collection of the single crystals, the ^{1}H NMR spectrum indicated the isolated material was pure, and when proper care was taken, the compound was characterized by mass spectral analysis. High-resolution FAB-MS: *m*/*z* calc 1248.813 (M^+), found 1248.817; calcd 1216.751 ($M^+ - 2CH_3$), found 1216.762.

Synthesis of [(2)Al$_4$Me$_8$] (7). A 2.0 M solution of trimethylaluminum in hexanes (593 μL, 1.186 mmol) was reacted with a solution of **2**H_4 (300 mg, 0.296 mmol) in 25 mL of pentane at 0 °C. The reaction was allowed to stirred for 1 h, and the solvent was removed in vacuo. The residue was dissolved in a minimal amount of CH_2Cl_2 (~5 mL) and cooled to −35 °C. After several days, colorless crystals formed and were isolated to give a yield of 287 mg (76%). Following this methodology, the addition of 2 equiv of trimethylaluminum to **2** afforded only a mixture of **6** and unreacted **2**. Anal. Calcd for $C_{78}H_{112}O_5Al_4\cdot{}^1/_2CH_2Cl_2$: C, 73.65; H, 8.90. Found C, 73.48; H, 8.91. ^{1}H NMR (CD_2Cl_2): δ 7.96 (d, dibenzofuran-*H*, J = 7.3 Hz, 2H), 7.37 (d, dibenzofuran-*H*, J = 7.3 Hz, 2H), 7.29 (t, dibenzofuran-*H*, J = 7.6 Hz, 2H), 7.21 (d, aryl-*H*, J = 2.5 Hz, 2H), 7.09 (d, aryl-*H*, J = 2.5 Hz, 2H), 7.02 (d, aryl-*H*, J = 2.5 Hz, 2H), 6.71 (d, aryl-*H*, J = 2.3 Hz, 2H), 5.90 (s, C*H*, 2H), 1.36 (s, *t*-Bu, 18H), 1.27 (s, *t*-Bu, 18H), 1.17 (s, *t*-Bu, 18H), 1.09 (s, *t*-Bu, 18H), 0.01 (s, AlCH_3, 6H), −0.51 (s, AlCH_3, 6H), −0.57 (s, AlCH_3, 6H), −1.18 (s, AlCH_3, 6H). ^{13}C NMR (CD_2Cl_2): δ 155.4, 152.8, 150.4, 147.2, 145.3, 140.9, 140.3, 137.6, 134.6, 132.4, 129.9, 129.0, 126.2, 125.4, 123.2, 122.8, 121.3, 119.6, 42.3, 35.6, 35.3, 34.8, 34.6, 32.2, 31.7, 31.4, 29.9, −4.6, −4.9, −9.2, −11.5. High-resolution FAB-MS: *m*/*z* calcd 1236.777 (M^+), found 1236.776.

Synthesis of [(3)Al$_2$Me$_2$] (8). A 2.0 M solution of trimethylaluminum in hexanes (148 μL, 0.296 mmol) was added to **3**H_4 (156 mg, 0.148 mmol) in 25 mL of toluene. The solution was stirred at ambient temperature for 3 h. The solvent was removed under vacuum, redissolved in 5 mL of dichloromethane, and cooled to −35 °C. Crystals formed over a period of a few days, and they were collected and dried to afford 110 mg (63%) of product. Anal. Calcd for $C_{75}H_{100}O_5Al_2\cdot{}^1/_2CH_2Cl_2$: C, 77.00; H, 8.65. Found: C, 76.51; H, 8.65. ^{1}H NMR (C_6D_6): δ 8.38 (d, aryl-*H*, J = 2.5 Hz, 2H), 8.23 (s, *CH*, 2H), 7.91 (d, xanthene-*H*, J = 6.5 Hz, 2H), 7.56 (d, aryl-*H*, J = 2.7 Hz, 2H), 7.12 (d, aryl-*H*, J = 2.7 Hz, 2H), 7.08 (d, aryl-*H*, J = 2.5 Hz, 2H), 6.99 (t, xanthene-*H*, J = 7.8 Hz, 2H), 6.85 (dd, xanthene-*H*, J = 1.2 Hz, 7.8 Hz, 2H), 1.55 (s, *t*-Bu, 18H), 1.33 (s, *t*-Bu, 18H), 1.19 (s, *t*-Bu, 18H), 1.07 (s, *t*-Bu, 18H), 1.03 (s, xanthene-CH_3, 6H), −0.31 (s, AlCH_3, 6H). ^{13}C NMR (C_6D_6): δ 151.6, 151.2, 147.0, 146.9, 141.3, 140.7, 138.1, 136.6, 135.1, 133.5, 132.9, 127.3, 126.6, 124.8, 124.3, 122.6, 122.4, 122.1, 37.3, 36.8, 36.0, 35.6, 35.1, 34.7, 33.6, 32.1, 31.9, 30.7, 29.4, −6.86. ^{27}Al NMR (C_6D_6): δ 60 ppm, $\omega_{1/2}$ 4.3 kHz.

Synthesis of [(1)Al$_2$Me$_2$] (9). A 2.0 M solution of trimethylaluminum in hexanes (500 μL, 1.00 mmol) was added to **1**H_4 (512 mg, 0.50 mmol) in 25 mL of toluene. The solution was heated at 80 °C for 3 h. The solvent was removed under vacuum, redissolved in minimum amount of pentane (~5 mL), and cooled to −35 °C. Crystals formed over a period of a few days and they were collected and dried to yield 294 mg of a pale green crystalline solid (53%). ^{1}H NMR (C_6D_6): δ 11.15 (s, anthracene-*H*, 1H), 9.11 (s, anthracene-*H*, 1H), 8.88 (d, aryl-*H*, J = 2.5 Hz, 2H), 8.23 (d, anthracene-*H*, J = 6.9 Hz, 2H), 7.68 (s, C*H*, 2H), 7.67 (d, aryl-*H*, J = 2.5 Hz, 4H), 7.46 (d, anthracene-*H*, J = 8.4 Hz, 2H), 7.31 (dd, anthracene-*H*, J = 6.9 Hz, 8.5 Hz, 2H), 7.01 (d, aryl-*H*, J = 2.5 Hz, 2H), 1.57 (s, *t*-Bu, 18H), 1.49 (s, *t*-Bu, 18H), 1.17 (s, *t*-Bu, 18H), 1.01 (s, *t*-Bu, 18H), −0.32 (s, AlCH_3, 6H). ^{13}C NMR (C_6D_6): δ 150.4, 148.0, 147.8, 143.0, 142.1, 140.8, 138.9, 136.6, 135.7, 132.7, 131.9, 127.0, 126.5, 125.6, 125.1, 124.9, 124.6, 124.3, 123.3, 122.4, 38.1, 37.0, 35.6, 35.2, 34.8, 33.7, 32.1, 32.0, 30.7, −6.3. ^{27}Al NMR (C_6D_6): δ 68 ppm $\omega_{1/2}$ 5.8 kHz. Single crystals of **9** slowly turned dark green over the course of several hours at room temperature, and this decomposition hampered all attempts to obtain acceptable elemental analysis data for the compound. If the material was kept at −35 °C, it was stable for several weeks and it could be used for further reactions. Moreover, satisfactory high-resolution mass spectral data could be obtained from single crystals if analyzed soon after warming to room temperature. High-resolution FAB-MS: *m*/*z* calcd 1102.694 (M^+), found 1102.690.

Synthesis of [(2)Al$_2$Me$_2$] (10). A solution of 2.0 M trimethylaluminum (506 μL, 1.01 mmol) in hexanes was added to **2**H_4 (500 mg, 0.49 mmol) in 25 mL of toluene. The solution was heated at reflux for 16 h, and the solvent was removed in vacuo. The residue was treated with 10 mL of pentane, and the resultant white solid was collected and dried to give 388 mg (67%) of product. Crystalline material suitable for X-ray and elemental analysis was obtained from a saturated CH_2Cl_2 solution at −35 °C. Anal. Calcd for $C_{72}H_{98}O_5Al_2\cdot CH_2Cl_2$: C, 74.15; H, 8.52. Found: C, 74.62; H, 8.42. ^{1}H NMR (C_6D_6): δ 8.37 (d, aryl-*H*, J = 2.4 Hz, 1H), 8.29 (d, dibenzofuran-*H*, J = 7.4 Hz, 1H), 8.16 (d, aryl-*H*, J = 2.3 Hz, 1H), 7.99 (d, dibenzofuran-*H*, J = 7.6 Hz, 1H), 7.31 (d, aryl-*H*, J = 2.4 Hz, 1H), 7.30 (s, *CH*, 1H), 7.29 (d, aryl-*H*, J = 2.5 Hz, 2H), 7.22 (d, aryl-*H*, J = 2.6 Hz, 1H), 7.00 (dd, dibenzofuran-*H*, J = 8.1 Hz, 1.0 Hz, 1H), 6.96 (t, dibenzofuran-*H*, J = 7.5 Hz, 1H), 6.85 (dd, dibenzofuran-*H*, J = 7.5 Hz, 1.0 Hz, 1H), 6.82 (m, dibenzofuran-*H* and *CH*, 2H), 6.78 (d, aryl-*H*, J = 2.4 Hz, 1H), 6.62 (d, aryl-*H*, J = 2.6 Hz, 1H,), 1.36 (s, *t*-Bu, 9H), 1.29 (s, *t*-Bu, 9H), 1.25 (s, *t*-Bu, 9H), 1.20 (s, *t*-Bu, 9H), 1.00 (s, *t*-Bu, 9H), 0.89 (s, *t*-Bu, 9H), 0.81 (s, *t*-Bu, 9H), 0.70 (s, *t*-Bu, 9H), 0.61 (s, AlCH_3, 3H), −0.92 (s, AlCH_3, 3H). ^{13}C NMR (C_6D_6): δ 155.1, 154.5, 153.6, 152.1, 150.7, 147.9, 145.6, 141.5, 141.1, 140.3, 140.1, 138.0, 137.8, 137.6, 137.5, 133.6, 130.8, 129.9, 129.7, 129.3, 128.7, 128.5, 127.4, 126.1, 125.6, 124.9, 124.1, 123.8, 123.7, 123.0, 122.8, 122.5, 122.4, 121.9, 119.4, 119.2, 40.3, 37.9, 35.6, 35.5, 35.3, 34.8, 34.7, 34.2, 33.8, 32.0, 31.8, 31.6, 31.5, 31.2, 31.1, 30.9, 30.7, 30.3, −8.4, −10.9.

Synthesis of [NEt$_4$][(1)Al$_2$Me$_2$Cl] (11). A solution of NEt_4Cl (14.9 mg, 0.090 mmol) in 0.5 mL of CH_2Cl_2 was added to a solution of crystalline **9** (100 mg, 0.090 mmol) in 4.5 mL of pentane. A precipitate formed, and the reaction was allowed to stir overnight. The solid was collected, dried, and recrystallized from a pentane/dichloromethane diffusion at −35 °C to yield 92 mg (75%) of a white microcrystalline product. Anal. Calcd for $C_{82}H_{116}NAl_2ClO_4\cdot CH_2Cl_2$: C 73.62; H, 8.78; N, 1.03. Found: C, 73.76; H, 9.03; N, 1.12. ^{1}H NMR (CD_2Cl_2): δ 9.05 (s, anthracene-*H*, 1H), 8.44 (s, anthracene-*H*, 1H), 7.85 (d, anthracene-*H*, J = 8.1 Hz, 2H), 7.79 (d, anthracene-*H*, J = 7.4 Hz, 2H), 7.35 (dd, anthracene-*H*, J = 7.4, 8.1 Hz, 2H), 7.01 (s, C*H*, 2H), 6.90 (d, aryl-*H*, J = 2.4 Hz, 4H), 6.49 (d, aryl-*H*, J = 2.4 Hz, 4H), 2.46 (q, N(CH_2CH$_3$)$_4$, J = 7.2 Hz, 8H), 1.27 (s, *t*-Bu, 36H), 1.01 (s, *t*-Bu, 36H), 0.69 (t, N(CH$_2$CH_3)$_4$, J = 7.2 Hz, 12H), −0.37 (s, AlCH_3, 6H). ^{13}C NMR (CD_2Cl_2): δ 154.0, 141.0, 138.5, 137.1, 134.5, 132.7, 132.5, 128.6, 128.4, 127.3, 125.0, 124.6, 121.5, 120.8, 52.8, 41.8, 35.4, 34.3, 31.8, 30.7, 7.5, −8.9. ^{27}Al NMR (C_7D_8): δ 60 ppm, $\omega_{1/2}$ 4.1 kHz.

Synthesis of [NEt_4][(2)Al_2Me_2Cl] (12). A solution of NEt_4Cl (8.2 mg, 0.050 mmol) in 0.5 mL of CH_2Cl_2 was added to a solution of crystalline **10** (55 mg, 0.050 mmol) in 4.5 mL of pentane. The resulting suspension was allowed to stir overnight. The solid was collected by filtration and recrystallized from a pentane/dichloromethane diffusion at −35 °C to yield 47 mg (69%) of a white solid. Anal. Calcd for $C_{80}H_{114}NAl_2ClO_5\cdot 1^1/_4CH_2Cl_2$: C, 71.92; H, 8.65; N, 1.03. Found: C, 71.45; H, 8.79; N, 1.03. ^{1}H NMR (CD_2Cl_2): δ 8.28 (d, dibenzofuran-*H*, $J = 8.1$ Hz, 2H), 7.80 (d, dibenzofuran-*H*, $J = 7.4$ Hz, 2H), 7.43 (dd, dibenzofuran-*H*, $J = 7.4$, 8.1 Hz, 2H), 7.33 (d, aryl-*H*, $J = 2.4$ Hz, 4H), 7.05 (d, aryl-*H*, $J = 2.4$ Hz, 4H), 6.80 (s, C*H*, 2H), 2.66 (q, $N(CH_2CH_3)_4$, $J = 7.2$ Hz, 8H), 1.37 (s, *t*-Bu, 36H), 1.21 (s, *t*-Bu, 36H), 0.92 (t, $N(CH_2CH_3)_4$, $J = 7.2$ Hz, 12H), −0.52 (s, $AlCH_3$,6H). ^{13}C NMR (CD_2Cl_2): δ 155.3, 151.6, 142.0, 137.6, 130.6, 128.6, 127.7, 124.9, 124.8, 122.7, 122.4, 119.0, 53.2, 39.5, 35.5, 34.7, 31.9, 30.5, 7.9, −6.9. ^{27}Al NMR (CD_2Cl_2): δ 67 ppm, $\omega_{1/2}$ 3.7 kHz.

Synthesis of [NEt_4]$_2$[(3)$Al_2Me_2Cl_2$] (13). A solution of NEt_4Cl (15 mg, 0.088 mmol) in 0.5 mL of CH_2Cl_2 was added to a solution of crystalline **8** (50 mg, 0.044 mmol) in 4.5 mL of pentane. The resulting suspension was allowed to stir overnight. The solid was collected by filtration, dried, and recrystallized from pentane/dichloromethane to yield 43 mg (63%) of a white solid. Addition of a single equivalent of NEt_4Cl to solutions of **8** resulted in the formation of a mixture of **13** and **8.** Single crystals for X-ray analysis were grown from a saturated dichloromethane/pentane solution containing several drops of toluene. Anal. Calcd for $C_{91}H_{140}N_2Al_2Cl_2O_5\cdot CH_2Cl_2$: C 71.20; H, 9.22; N, 1.81. Found: C, 70.84; H, 9.31; N, 2.05. ^{1}H NMR (CD_2Cl_2): δ 7.52 (d, xanthene-*H*, $J = 7.5$ Hz, 1H), 7.22 (d, xanthene-*H*, $J = 7.8$ Hz, 1H), 7.16 (d, aryl-*H*, $J = 2.1$ Hz, 1H), 7.12 (d, xanthene-*H*, $J = 7.8$ Hz, 1H), 7.05 (d, aryl-*H*, $J = 2.4$ Hz, 1H), 7.02 (d, aryl-*H*, $J = 2.1$ Hz, 1H), 6.96 (d, aryl-*H*, $J = 2.4$ Hz, 1H), 6.88 (m, xanthene-*H*, 1H), 6.84 (d, aryl-*H*, $J = 2.4$ Hz, 1H), 6.79 (t, xanthene-*H*, $J = 7.8$ Hz, 1H), 6.59 (s, C*H*, 1H), 6.43 (d, xanthene-*H*, $J = 7.8$ Hz, 1H), 6.40 (s, C*H*, 1H), 6.34 (d, aryl-*H*, $J = 2.1$ Hz, 1H), 5.79 (d, aryl-*H*, $J = 2.4$ Hz, 1H), 5.47 (d, aryl-*H*, $J = 2.1$ Hz, 1H), 2.96 (q, NCH_2CH_3, $J = 7.2$ Hz, 16H), 1.62 (s, xanthene-Me, 3H), 1.50 (s, *t*-Bu, 9H), 1.46 (s, *t*-Bu, 9H), 1.42 (s, *t*-Bu, 9H), 1.37 (s, *t*-Bu, 9H), 1.29 (s, xanthene-Me, 9H), 1.26 (s, *t*-Bu, 9H), 1.10−1.04 (m, *t*-Bu and NCH_2CH_3, 31H), 1.00 (s, *t*-Bu, 9H), 0.93 (s, *t*-Bu, 9H), −0.78 (s, Al-CH_3, 3H), −1.95 (s, Al-CH_3, 3H). ^{13}C NMR (CD_2Cl_2): δ 157.1, 156.4, 155.8, 155.0, 149.9, 149.0, 138.3, 137.6, 137.1, 136.7, 136.6, 136.5, 136.3, 136.2, 135.5, 135.3, 135.2, 135.1, 133.5, 131.0, 130.5, 129.8, 128.3, 128.1, 127.8, 127.4, 125.9, 124.6, 123.8, 123.0, 122.8, 121.3, 120.9, 120.7, 120.5, 120.0, 53.3, 43.0, 37.9, 36.0, 35.8, 35.7, 35.4, 34.5, 34.4, 34.2, 34.1, 32.7, 32.6, 32.5, 32.4, 32.2, 32.1, 32.0, 31.7, 31.4, 31.3, 31.1, 30.7, −5.7. ^{27}Al NMR (CD_2Cl_2): δ 56 ppm, $\omega_{1/2}$ 3.7 kHz.

Synthesis of [(1)Al_2Me_2(OPh)Na(OEt_2)] (14). A solution of crystalline **9** (150 mg, 0.136 mmol) in 4 mL of CH_2Cl_2 was added to a slurry of NaOPh (15.8 mg, 0.136 mmol) in 1 mL of diethyl ether. The mixture was allowed to stir overnight, and the volume was reduced to 1 mL. Additional ether (few drops) was added, and the solution was stored at −35 °C overnight to allow for crystallization. After 24 h, the crystalline solid was collected by filtration and dried to afford 58 mg (32%) of colorless crystals. Anal. Calcd for $C_{84}H_{111}Al_2NaO_6\cdot ^1/_2CH_2Cl_2$: C, 75.96; H, 8.45. Found: C, 75.38; H, 8.62. ^{1}H NMR (C_6D_6): δ 10.14 (s, anthracene-*H*, 1H), 8.42 (d, anthracene-*H*, $J = 6.9$ Hz, 2H), 8.16 (s, anthracene-*H*, 1H), 7.67 (s, C*H*, 2H), 7.65 (d, anthracene-*H*, 2H), 7.40 (m, anthracene-*H*, 2H and phenoxide-*H*, 2H), 7.23 (2, aryl-*H*, 2H), 7.18 (m, aryl-*H*, 2H), 7.11 (s, aryl-*H*, 2H), 7.02 (s, aryl-*H*, 2H), 6.77 (t, phenoxide-*H*, $J = 7.5$ Hz, 1H), 6.35 (t, phenoxide-*H*, $J = 7.5$ Hz, 1H), 5.91 (t, phenoxide-*H*, $J = 7.5$ Hz, 1H), 2.34 (q, $O(CH_2CH_3)_2$, $J = 6.9$ Hz, 4H), 1.54 (s, *t*-Bu, 18H), 1.21 (s, *t*-Bu, 36H), 1.08 (s, *t*-Bu, 18H), 0.24 (t, $O(CH_2CH_3)_2$, $J = 6.9$ Hz, 6H), 0.21 (s, $AlCH_3$, 6H). ^{13}C NMR (C_6D_6): δ 154.5, 151.2, 151.0, 142.9, 142.5, 139.4, 138.4, 138.0, 137.9, 136.9, 133.1, 133.0, 132.9, 131.1, 130.2, 129.4, 127.8, 127.3, 125.6, 124.8, 124.2, 124.1, 123.2, 122.9, 121.9, 114.7, 65.4, 39.9, 36.5, 35.5, 34.8, 34.6, 32.8, 32.3, 31.8, 30.5, 14.5, −7.8.

Synthesis of {(1)[AlMe($OC_{11}H_{14}$)]$_2$} (15). A solution of α,α,α-trimethylacetophenone (60.0 μL, 0.354 mmol) in 1 mL of CH_2Cl_2 was added to a solution of crystalline **9** (195 mg, 0.177 mmol) in 10 mL of pentane. The resulting suspension was allowed to stir overnight, and the precipitate was isolated to yield 101 mg (40%). Crystals were obtained from a dichloromethane/pentane solution at −35 °C for X-ray and elemental analysis. Even when a solution containing 1 equiv of α,α,α-trimethylacetophenone was reacted with **9**, the split structure complex **15** was isolated. Anal. Calcd for $C_{96}H_{124}Al_2O_6$: C, 80.75; H, 8.75. Found: C, 79.97; H, 9.12. ^{1}H NMR (C_6D_6): δ 8.22 (s, anthracene-*H*, 1H), 8.03 (s, anthracene-*H*, 1H), 7.85 (d, aryl-*H*, $J = 2.6$ Hz, 2H), 7.75 (m, aryl-*H*, 4H), 7.56 (d, aryl-*H*, $J = 2.7$ Hz, 2H), 7.32−7.18 (m, anthracene-*H*, 6H), 6.82 (t, acetophenone-*H*, $J = 7.2$ Hz, 4H), 6.67 (t, acetophenone-*H*, $J = 7.8$ Hz, 6H), 5.85 (s, *CH*, 2H), 1.87 (s, *t*-Bu, 18H), 1.59 (s, *t*-Bu, 18H), 1.34 (s, *t*-Bu, 18H), 0.91 (s, *t*-Bu, 18H), 0.64 (s, *t*-Bu, 18H), −0.49 (s, $AlCH_3$, 6H). ^{13}C NMR (C_6D_6): δ 233.0, 155.2, 155.0, 140.3, 139.7, 139.4, 139.1, 137.6, 135.0, 134.5, 133.8, 132.9, 132.1, 131.5, 130.7, 129.2, 128.9, 127.5, 126.8, 126.7, 125.9, 123.8, 123.0, 121.6, 120.4, 56.1, 46.0, 35.6, 35.4, 35.2, 35.1, 33.7, 32.8, 30.9, 30.3, 28.8, −9.0.

Synthesis of [(2H)Al(OC_5H_8)] (16). A solution of cyclopentanone (2.0 μL, 0.023 mmol) in 1 mL of CH_2Cl_2 was added to a solution of crystalline **9** (25.0 mg, 0.023 mmol) in 5 mL of pentane. The resulting mixture was allowed to stir overnight, during which time a white solid precipitated out of solution. The solid was collected and washed with pentane to yield 10.0 mg (37%) of a white product. Single crystals for structural and elemental analysis were obtained from saturated dichloromethane solutions at −35 °C. Anal. Calcd for $C_{75}H_{97}AlO_6\cdot ^3/_4CH_2Cl_2$: C 76.76; H, 8.38. Found: C, 76.22; H, 8.74. ^{1}H NMR (C_6D_6): δ 8.66 (s, *CH*, 1H), 8.64 (d, aryl-*H*, $J = 2.1$, 1H), 7.76 (d, aryl-*H*, $J = 2.4$ Hz, 1H), 7.61 (d, aryl-*H*, $J = 2.4$ Hz, 1H), 7.58 (s, *CH*, 1H), 7.54 (d, aryl-*H*, $J = 2.1$ Hz, 1H), 7.46 (d, aryl-*H*, $J = 2.7$ Hz, 1H), 7.42 (br s, aryl-*H*, 1H), 7.37 (br s, aryl-*H*, 1H), 7.35−7.16 (m, aryl-*H* and dibenzofuran-*H*, 6H), 6.89 (t, dibenzofuran-*H*, $J = 7.6$ Hz, 1H), 5.01 (s, O*H*, 1H), 2.4−2.1 (m, cyclopentanone-*H*, 8H), 1.76 (s, *t*-Bu, 9H), 1.60 (s, *t*-Bu, 9H), 1.56 (s, *t*-Bu, 9H), 1.48 (s, *t*-Bu, 9H), 1.44 (s, *t*-Bu, 9H), 1.30 (s, *t*-Bu, 9H), 1.26 (s, *t*-Bu, 9H), 0.68 (s, *t*-Bu, 9H). ^{13}C NMR (C_6D_6): δ 239.2, 156.1, 154.6, 154.2, 153.9, 152.7, 152.4, 151.9, 151.6, 141.2, 140.8, 140.6, 140.5, 139.6, 137.8, 137.2, 137.0, 135.5, 132.2, 130.4, 130.3, 126.5, 125.8, 125.0, 124.5, 124.4, 124.2, 123.9, 123.5, 123.3, 123.2, 123.1, 123.0, 122.5, 121.9, 120.4, 119.5, 43.0, 41.0, 39.6, 37.5, 36.2, 36.1, 35.9, 35.8, 35.1, 34.9, 34.7, 34.6, 32.5, 32.4, 32.1, 32.0, 31.4, 31.1, 31.0, 30.8.

Synthesis of [(4)Al_3Me_5] (17). A 2.0 M solution of trimethylaluminum in hexanes (831 μL, 1.66 mmol) was added to **4**H_4 (470 mg, 0.554 mmol) in 25 mL of pentane at ambient temperature. The solution was allowed to react for 1 h, and the solvent was removed. The residue was treated with 2 mL of dichloromethane and cooled to −35 °C. Crystalline material formed after several days and the product was collected, washed with cold pentane, and dried to yield 370 mg (63%) of white crystals. Despite repeated attempts to isolate a binuclear species by using reduced equivalents of trimethylaluminum, the only products identifiable in the ^{1}H NMR spectra of the reaction mixtures were **4**H_4 and the trinuclear complex, **17**. Anal. Calcd for $C_{63}H_{79}O_5Al_3\cdot ^3/_4CH_2Cl_2$: C, 72.17; H, 7.65. Found: C, 71.82; H, 8.33. ^{1}H NMR (C_6D_6): δ 8.78 (s, *CH*, 1H), 8.49 (d, dibenzofuran-H, $J = 7.5$ Hz, 1H), 8.42 (d, aryl-H, $J = 2.4$ Hz, 1H), 8.38 (d, dibenzofuran-H, $J = 7.5$ Hz, 1H), 8.29 (d, aryl-H, $J = 2.4$ Hz, 1H), 8.17 (d, aryl-H, $J = 2.4$ Hz, 1H), 7.89

(d, aryl-H, J = 2.1 Hz, 1H), 7.77 (s, C*H*, 1H), 7.36 (d, dibenzofuran-H, J = 7.7 Hz, 2H), 7.22 (dd, dibenzofuran-H, J = 7.5 Hz, 7.7 Hz, 2H), 7.15 (under solvent peak, 1H), 6.87 (d, aryl-H, J = 1.9 Hz, 1H), 6.85 (d, aryl-H, J = 1.9, 1H), 2.68 (s, Me, 3H), 2.52 (s, Me, 3H), 2.17 (s, Me, 3H), 2.07 (s, Me, 3H), 1.27 (s, *t*-Bu, 9H), 1.23 (s, *t*-Bu, 9H), 1.22 (s, *t*-Bu, 9H), 1.19 (s, *t*-Bu, 9H), 0.29 (s, AlC*H*$_3$, 3H), −0.21 (s, AlC*H*$_3$, 3H), −0.28 (s, AlC*H*$_3$, 3H), −1.38 (s, AlC*H*$_3$, 3H), −1.71 (s, AlC*H*$_3$, 3H). ^{13}C NMR (C_6D_6): δ 155.8, 154.6, 151.5, 150.1, 148.8, 148.4, 148.2, 143.9, 142.0, 140.1, 138.2, 135.8, 134.2, 133.7, 133.5, 131.0, 130.9, 129.7, 128.9, 128.7, 127.8, 127.5, 127.3, 127.2, 126.9, 126.2, 126.0, 125.8, 125.0, 124.9, 123.9, 123.8, 123.3, 122.9, 120.8, 119.9, 38.2, 34.9, 34.8, 34.6, 32.3, 31.8, 31.7, 23.1, 21.8, 21.5, 20.0, 18.8, 18.2, 14.6, −2.9, −4.8, −12.1, −12.6.

Synthesis of [(5)Al$_2$Me$_2$] (18). A solution of 2.0 M trimethylaluminum (104 μL, 0.207 mmol) in hexanes was added to **5**H$_4$ (100 mg, 0.103 mmol) in 15 mL of pentane. The solution was stirred at ambient temperature for 5 h. The solvent was removed, and the residue was redissolved in a minimal amount of dichloromethane. The solution was stored for several days at −35 °C, and the resulting white crystalline material was collected and dried under vacuum to give 62 mg (53%) of **18**. Anal. Calcd for $C_{70}H_{88}O_4Al_2{\cdot}CH_2Cl_2$: C, 75.31; H, 8.01. Found: C, 75.39; H, 8.53. ^{1}H NMR (C_6D_6): δ 10.82 (s, anthracene-*H*, 1H), 8.90 (s, C*H*, 2H), 8.64 (d, anthracene-*H*, J = 7.5 Hz, 2H), 8.62 (br m, aryl-*H*, 4H), 7.76 (s, anthracene-*H*, 1H), 7.48 (d, anthracene-*H*, J = 7.7 Hz, 2H), 7.2−7.4 (br m, 6H), 3.67 (br m, C*H*(CH$_3$)$_2$, 4H), 1.34 (s, *t*-Bu, 36H), 1.32 (br s, CH(C*H*$_3$)$_2$, 24H), −0.19 (s, AlC*H*$_3$, 3H). ^{13}C NMR (C_6D_6): δ 141.0, 138.4, 132.6, 132.1, 127.4, 126.3, 125.4, 122.1, 120.5, 35.0, 32.1, 28.2, 24.2, −10.4.

Synthesis of {(5)[AlMe][AlMe(OCHPh)]} (19). A solution of benzaldehyde (23.0 μL, 0.226 mmol) in 1 mL of pentane (1 mL) was added to an in situ generated solution of **18** (232 mg, 0.226 mmol) in 5 mL of pentane. The resulting red mixture was allowed to stir overnight at ambient conditions. The volume was reduced to ~3 mL, and the reaction mixture was stored at −35 °C for several days. The microcrystalline solid was collected and washed with cold pentane to yield 37 mg (12%) of a red powder. The isolated yield was low primarily due to the high solubility of **19** in pentane even at −35 °C. Large single crystals suitable for X-ray and elemental analysis were obtained from a concentrated dichloromethane/pentane solution at −35 °C. Anal. Calcd for $C_{77}H_{94}Al_2O_5{\cdot}2^1/_2CH_2Cl_2$: C, 66.91; H, 7.31. Found: C, 69.81; H, 7.60. ^{1}H NMR (C_6D_6): δ 10.75 (s, anthracene-*H*, 1H), 8.66 (s, 1H), 8.56 (s, 2H), 8.50 (d, anthracene-*H*, J = 6.9 Hz, 2H), 7.58 (br s, aryl-*H*, 4H), 7.81 (br s, C$_6$H$_5$C*H*O, 1H), 7.32 (t, anthracene-*H*, J = 7.8 Hz, 1H), 7.25 (br s, aryl-*H*, 4H), 7.17−6.96 (m, anthracene-*H*, 3H), 6.67 (m, benzaldehyde-*H*, 2H), 6.26 (t, benzaldehyde-*H*, J = 7.3 Hz, 2H), 5.91 (br s, benzaldehyde-*H*, 2H), 3.69 (br m, C*H*CH$_3$, 4H), 1.35 (d, CHC*H*$_3$, 12H), 1.27 (br s, *t*-Bu and CHC*H*$_3$, 48H), −0.12 (br s, Al-Me, 6H). ^{13}C NMR (C_6D_6): δ 199vbr, 155.8, 154.0, 148.8, 147.3, 146.5, 145.5, 142.0, 141.8, 141.5, 141.2, 140.6, 139.9, 139.0, 138.3, 137.9, 137.3, 135.0, 133.2, 133.0, 132.5, 131.9, 130.9, 130.0, 129.8, 129.7, 129.0, 128.9, 127.7, 127.1, 126.6, 126.4, 126.0, 124.1, 123.7, 123.1, 122.8, 121.7, 120.5, 120.3, 119.9, 81.3, 42.6, 34.9, 34.6, 34.3, 32.3, 31.9, 31.5, 31.3, 28.7, 28.6, 27.2, 25.4, 24.7, 24.6, 24.5, 23.8, 23.7, 23.1, 22.9, 22.4, 21.8, 14.6, −10.8, −11.9.

Xray-Crystallgraphy. Unit cell dimensions and intensity data (Tables 1 and 4) for all the structures were obtained on a Siemens CCD SMART diffractometer at −100 °C, with monochromatic Mo Kα X-rays (λ = 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.[41] 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 and bridging methyl hydrogen atoms, 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 contributions to the diffraction were removed ("squeezed") from the data by the Platon for Windows software program.[42] The experimental data for structures of **1**−**4** as well as descriptions of the refinements for all compounds are contained in the Supporting Information.

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Supporting Information Available: Experimental details and crystallographic data for compounds **1**−**17** and **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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