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Simultaneous Coordination of a Nucleophile with a Bifunctional Lewis Acid Assembly Incorporating a Linked Phenoxide Ligand System

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*Summary: Addition of 4,4′,4′′,4′′′-tetra-tert-butyl-6,6′,6′′,6′′′-tetra-tert-butyl-2,2′,2′′,2′′′-(1,8-anthracenemethanediyl)-tetraphenol (**1**) to a solution of Al_2Me_6 affords a tetranuclear aluminum species (**2**) which, upon heating, formed a binuclear species (**3**). Treatment of **3** with NEt_4Cl allowed for the isolation of **4**, a discrete bimetallic aluminum assembly wherein the two metals simultaneously coordinate an external nucleophile.*

Although ligand systems containing multiple Lewis basic sites have been widely utilized for applications ranging from molecular recognition to catalysis,[1] analogous molecules containing multiple Lewis acidic sites have proven to be remarkably more difficult to prepare. Consequently, despite the vast potential for this class of molecule, their chemistry has been relatively underdeveloped. Recently, particular emphasis has been placed on the incorporation of two Lewis acidic metals into simple complexes,[2] since if two metal centers can be made to work in consort on nucleophilic substrates, the ensuing catalysts should greatly influence, and perhaps significantly enhance, reactivity. Despite this effort, only a few examples of well-defined, multinuclear, Lewis acidic complexes capable of simultaneous coordination of an external nucleophile are known, and the majority have involved the complexation of anionic ligands[3−5] or utilized mercury, a relatively soft Lewis acid.[2b,6−10] With harder Lewis acids such as aluminum, the synchronized interaction of two metal centers with a coordinated substrate should result in the generation of a reactive species with potentially important utility. Indeed, several interesting catalytic reactions have been postulated to proceed via a pathway involving the simultaneous coordination of a carbonyl group by two aluminum centers,[11] but the isolation of discrete catalytic species with these hard Lewis acids has remained quite elusive unless the carbonyl group is incorporated directly into the ligand backbone.[12,13] Additionally, bifunctional Lewis acidic complexes may be used to remove ligands such as chloride or alkyl groups from transition metals to afford cationic catalysts useful in olefin polymerizations.[14,15] With these concepts in mind, we have undertaken the development of ligand systems which place two Lewis acidic metals in close proximity, and herein we report the preparation and reactivity of a bimetallic aluminum complex.

Having witnessed a tendency for the oxygen atoms in phenolic ligands linked at the 2-position to a methylene group to align with respect to the methine hydrogen,[16] a simple strategy was employed for the preparation of a tetraphenoxide ligand, **1**, in which two sets of 2,2′-methylenebis(4,6-di-*tert*-butylphenol) groups are linked to the 1- and 8-positions of an anthracene spacer.[17] With *tert*-butyl groups at the *para* position of the phenol to provide steric bulk and the predilection of the phenolic arms to be congruent with the hydrogen atom on the linking methine, we reasoned the two sets

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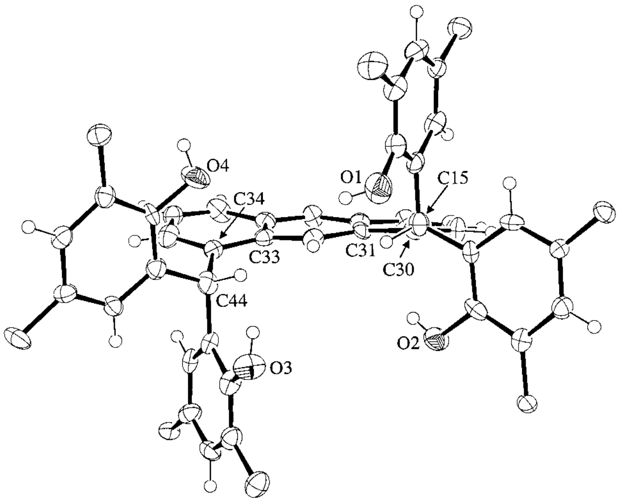

Figure 1. ORTEP diagram (30% probability ellipsoids) of **1**, 4,4′,4″,4‴-tetra-*tert*-butyl-6,6′,6″,6‴-tetra-*tert*-butyl-2,2′,2″,2‴-(1,8-anthracenemethanediyl)tetraphenol. The *tert*-butyl methyl groups have been omitted for clarity.

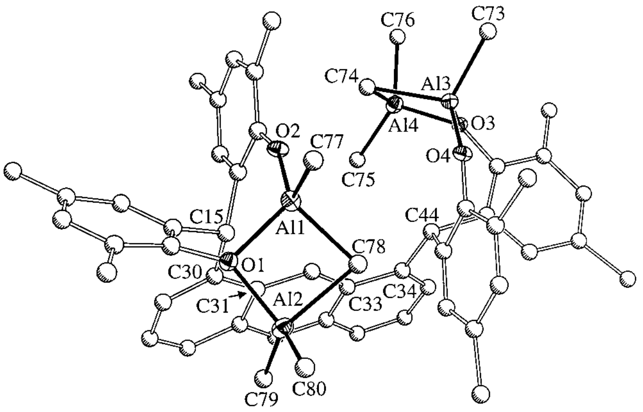

Figure 2. Structure of **2** (30% probability ellipsoids for Al and O atoms; carbon atoms drawn with arbitrary radii). For clarity, the *tert*-butyl methyl groups and all hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg): Al(1)−O(2) = 1.705(3), Al(1)−O(1) = 1.859(3), Al(1)−C(77) = 1.930(5), Al(1)−C(78) = 2.066(6), Al(2)−O(1) = 1.850(3), Al(2)−C(79) = 1.943(5), Al(2)−C(78) = 2.163(6); O(2)−Al(1)−O(1) = 112.16(15), Al(2)−O(1)−Al(1) = 96.05(14).

of bis(phenol)methylene groups would point toward each other, and the solid-state structure confirmed this predisposition (Figure 1). Moreover, given the utility of reagents such as methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) for organic transformations,[18] complexes with properties similar to MAD may result when the two sets of oxygen donors in **1** each coordinate an aluminum center. Accordingly, if bidentate binding could be achieved with this type of complex, the resulting catalysts should be particularly effective.

Initial reactions of **1** with trimethylaluminum at room temperature afforded a species containing four aluminum centers, **2**, which was isolated as a crystalline solid in 63% yield.[19] As can be seen in Figure 2, the compound is C_2 symmetric, 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. Inclusion of this phenolic bridge in the dimeric structure increases the Al(1)−Al(2) separation to 2.757(2) Å in **2** as compared to the value of 2.606(2) Å found in Al_2Me_6,[20] and unlike Al_2Me_6, there is a pronounced asymmetry in the methyl bridge in **2** with distances of 2.066(6) and 2.163(6) Å to Al(1) and Al(2), respectively. Surprisingly, despite the complexity of the tetranuclear structure, the anthracene linker exhibits only a slight bend of 4.5° between the planes defined by C(15)−C(30)−C(31) and C(44)−C(34)−C(33).

In principle, the tetrametallic structure in **2** contains two $AlMe_3$ units joined at the periphery to the desired bimetallic species, and indeed, heating a toluene solution of **2** in the presence of an additional 1 equiv of **1** induced the extrusion of 2 equiv of $AlMe_3$. Cooling a pentane solution of the product to −35 °C allowed for the isolation of the highly crystalline, C_2-symmetric, bimetallic complex **3**, depicted in Figure 3.[21] Rather than adopting a three-coordinate geometry akin to MAD, the proximity of the phenolic donors and their propensity to bridge between metal centers allows for the assembly of the familiar Al_2O_2 unit wherein the two metal centers are linked symmetrically by two phenoxide groups.[22,23] With an Al···Al separation of 2.834(2) Å, the Al_2O_2 bridge unit is unexceptional, but its formation apparently comes at the expense of a distortion in the anthracene backbone, exemplified by the 31.8° angle between the C(15)−C(30)−C(31) and C(44)−C(34)−C(33) planes.

Perhaps due in some part to the unfavorable deformation induced in the anthracene backbone, the Al_2O_2 unit in **3** was susceptible to attack by nucleophiles and addition of one equivalent of NEt_4Cl disrupted the two phenolic bridges, affording a new bimetallic, anionic species, **4**, wherein a chloride atom straddles the two metal sites. As depicted in Figure 4,[24] the geometry

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(17) (a) The synthesis was adapted from: Grüttner, C.; Böhmer, V.; Assmus, R.; Scherf, S. *J. Chem. Soc., Perkin Trans. 1* **1995**, 93−94. (b) 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. (c) Crystal data for $\mathbf{1}\cdot 2H_2O\cdot C_5H_{12}$, $C_{77}H_{126}O_6$: M_w = 1147.78, triclinic, space group $P\bar{1}$, a = 14.4377(12) Å, b = 15.1326(13) Å, c = 15.7110(14) Å, α = 77.820(2)°, β = 86.244(2)°, γ = 80.759(2)°, V = 3309.9(5) Å^3, Z = 2, T = 173(2) K, R1 = 0.0962 ($I > 2\sigma(I)$), and wR2 = 0.2375 for 11 264 independent reflections. Complete experimental data can be found in the Supporting Information.

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(19) Crystal data for $\mathbf{2}\cdot 2C_5H_{12}$, $C_{90}H_{138}O_4Al_4$: M_w = 1391.92, triclinic, space group $P\bar{1}$, a = 13.6213(7) Å, b = 17.3859(9) Å, c = 21.1789(11) Å, α = 111.891(1)°, β = 98.218(1)°, γ = 101.501(1)°, V = 4428.3 (4) Å^3, Z = 2, T = 173(2) K, R1 = 0.0912 ($I > 2\sigma(I)$), and wR2 = 0.2510 for 13 827 independent reflections. ^{1}H NMR (C_6D_6): δ −1.10 (s, AlCH_3, 6H), −0.17 (s, AlCH_3, 6H), −0.03 (s, AlCH_3, 6H), 0.37 (s, AlCH_3, 6H). Complete experimental data can be found in the Supporting Information.

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(21) Crystal data for $\mathbf{3}\cdot 3C_5H_{12}$, $C_{89}H_{132}O_4Al_2$: M_w = 1319.91, triclinic, space group $P\bar{1}$, a = 13.652(4) Å, b = 15.532(5) Å, c = 21.088(6) Å, α = 72.037(5)°, β = 77.508(6)°, γ = 82.443(6)°, V = 4143(2) Å^3, Z = 2, T = 173(2) K, R1 = 0.0890 ($I > 2\sigma(I)$), and wR2 = 0.2480 for 11 472 independent reflections. ^{1}H NMR (C_6D_6): δ −0.32 (s, AlCH_3, 6H). Complete experimental data can be found in the Supporting Information.

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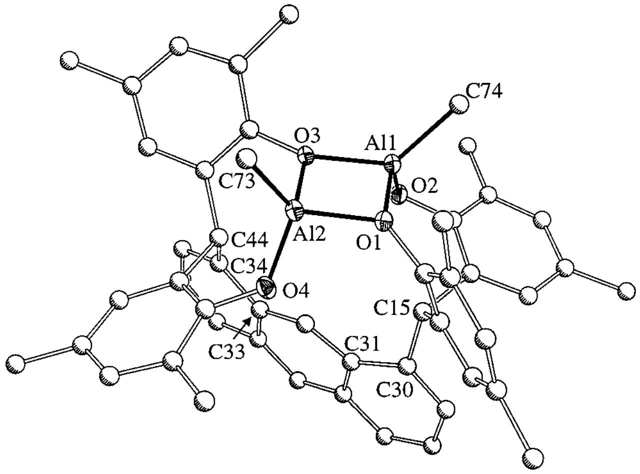

Figure 3. Structure of **3** (30% probability ellipsoids for Al and O atoms; carbon atoms drawn with arbitrary radii). For clarity, the *tert*-butyl methyl groups and all hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg): Al(1)−O(2) = 1.720(4), Al(1)−O(3) = 1.857(3), Al(1)−O(1) = 1.883(3), Al(1)−C(74) = 1.950(5), O(3)−Al(1)−O(1) = 81.48(14), Al(2)−O(1)−Al(1) = 98.36(15).

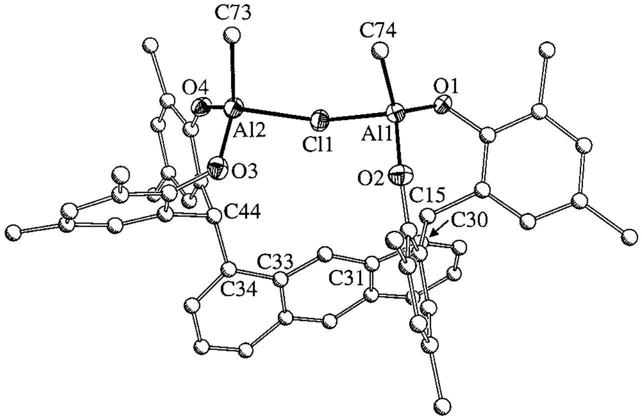

Figure 4. Structure of **4** (30% probability ellipsoids for Al, O, and Cl atoms; carbon atoms drawn with arbitrary radii). For clarity, the tetraethylammonium cation, *tert*-butyl methyl groups, and all hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg): Al(1)−Cl(1) = 2.3139(11), Al(2)−Cl(1) = 2.3224(11), Al(1)−O(2) = 1.713(2), Al(1)−O(1) = 1.762(2), Al(1)−C(74) = 1.932(3); Al(1)−Cl(1)−Al(2) = 118.70(4).

about the aluminum sites relative to **3** is closer to an idealized tetrahedron with angles ranging from 98.69(7) to 119.75(14)°. To insert the chloride atom between the two metal centers, the Al···Al separation has increased by more than 1 Å relative to **3** to a distance of 3.9886(12) Å, further highlighting the flexibility of **1**. The anthracene backbone once again significantly distorts from planarity, and the angle between the C(15)−C(30)−C(31) and C(44)−C(34)−C(33) planes has increased considerably relative to **3** to 45.7°. The remaining geometric parameters are unremarkable, except for a small decrease in the average Al−Cl distance to 2.318(1) Å in comparison to similar chloride-bridged complexes such as $[Me_3AlClAlMe_3]^-$ (Al−Cl(av) = 2.363 Å)[25] and $[(MeC)_4N(Me)_2AlClAl(Me)_2N(CMe)_4]^-$ (Al−Cl(av) = 2.335 Å).[26]

In the solid state, the Al−Cl−Al unit extends out over one side of the anthracene, inducing asymmetry between the two arms in the 2,2′-methylenebis(4,6-di-*tert*-butylphenol) groups, but in solution, the position of the chloride atom appears to rapidly equilibrate between both sides of the anthracene spacer, since all four phenol groups are equivalent over a wide temperature range (−80 to +80 °C) in the ^{1}H NMR spectrum of **4**. The low-temperature ^{1}H NMR (−80 °C) 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 to relaxation by the Al quadrupole at low temperatures, and not rapid exchange of the chloride ion between the two metal centers. 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) and only one resonance was observed (δ 60, $\omega_{1/2}$ = 4100 Hz, room temperature), consistent with a four-coordinate aluminum center with two aryloxide donors.[27,28]

In conclusion, a new tetraphenolic ligand system has been designed to hold two aluminum centers in close proximity to allow for cooperative binding, and the conversion of **3** to **4** represents a rare example of bidentate binding of an *external* nucleophile through a single-atom bridge by a discrete *bimetallic* aluminum assembly.[25,26] Although other nucleophiles such as phenoxide ion will form bridged species analogous to **4**,[29] all attempts to isolate a bridged complex with simple carbonyl substrates have been unsuccessful to date. Fortunately, simple alterations in the synthetic procedure utilized for the preparation of **1** allows for the fine-tuning of the tetraphenolic ligand system. Along with efforts to adjust the constraints of the ligand system to induce cooperative binding of carbonyl groups, investigations into the catalytic activity of the complexes are currently underway.

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Supporting Information Available: Text, figures, and tables giving complete experimental details and crystallographic data (excluding structure factors) for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Crystal data for $\mathbf{4}\cdot CH_2Cl_2\cdot C_5H_{12}$, $C_{87}H_{128}O_4Al_2Cl_3N$: M_w = 1413.46, monoclinic, space group $P2_1/c$, a = 15.1245(7) Å, b = 21.2736(10) Å, c = 26.0590(11) Å, β = 95.246(1)°, V = 8349.4(7) Å^3, Z = 4, T = 173(2) K, R1 = 0.0660 ($I > 2\sigma(I)$), and wR2 = 0.2001 for 14 664 independent reflections. ^{1}H NMR (CD_2Cl_2): δ −0.37 (s, AlCH_3, 6H). Complete experimental data can be found in the Supporting Information.

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(27) Chemical shifts of aluminium species are highly dependent on the electronic environment *as well as* the coordination number: Barron, A. R. *Polyhedron* **1995**, *14*, 3197−3207.

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