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Synthesis and Characterization of Heterobimetallic Al−O−Cu Complexes toward Models for Heterogeneous Catalysts on Metal Oxide Surfaces

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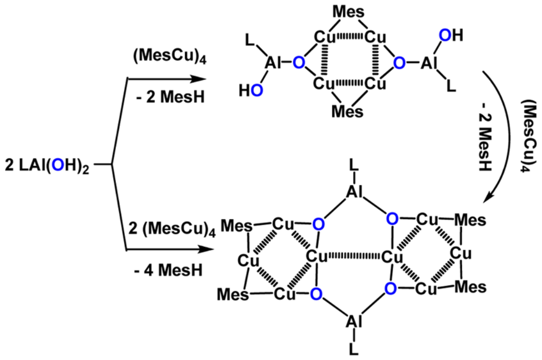
S *Supporting Information*



ABSTRACT: The β-diketiminato aluminum-monohydroxide and -dihydroxide were reacted with tetrameric $(CuMes)_4$ (Mes = 2,4,6-$Me_3C_6H_2$) to prepare Cu(I) complexes bearing the Al−O−Cu moiety. All complexes are characterized by elemental analysis, nuclear magnetic resonance, and single-crystal X-ray diffraction. The reaction of aluminum−monohydroxide LAlR(OH) (L = $HC[C(Me)N(Ar)]_2$; Ar = 2,6-$i Pr_2C_6H_3$; R = Me, Et) with $(CuMes)_4$ afforded the Cu(I) alumoxane $[LAl(R)OCu\cdot MesCu]_2$ (R = Me, **1**; Et, **2**). Using the aluminum-dihydroxide $LAl(OH)_2$ as the precursor, the dimeric $[LAl(OH)OCu\cdot MesCu]_2$ (**3**) was isolated, bearing one reactive OH group on each Al center. When the reaction of $LAl(OH)_2$ with $(CuMes)_4$ was carried out at 70 °C, the dimeric octanuclear Cu(I) compound $[LAl(OCu\cdot MesCu)_2]_2$ (**4**) was formed, where two residual Mes groups are located at the neighboring position on each of the two $(OCu\cdot MesCu)_2$ squares. Compound **4** can be alternatively obtained by reacting **3** with 1 equiv of $(CuMes)_4$ to demonstrate the stepwise assembly of the Cu(I) alumoxanes.

1. INTRODUCTION

Heterogeneous catalysts consist of catalytically active components, which are very often deposited on a high surface area,[1] usually silica and aluminum oxide together with zeolites, alumosilicates, and active carbon function as supports.[2] The single-site heterogeneous catalysts are formed via anchoring complexes through hydroxyl groups on solid supports.[3] Especially, Ziegler−Natta polymerization systems have been greatly promoted by a rational design of modeling the commercial heterogeneous systems with well-defined homogeneous catalysts.[4] Soluble molecular analogues for the fixation of molecular catalysts on a metal oxide support were designed and constructed to contain the basic structural units of the proposed architectures of the heterogeneous metal oxide catalysts. We have employed organosilanetriols and organoaluminum monohydroxides to develop soluble metallasiloxanes with Si−O−M linkages[5] and the heterobimetallic oxides containing a Al−O−M moiety, respectively.[6] Some of these compounds have shown interesting catalytic properties in two phase hydroformylation of 1-hexene.[7a] The titanosiloxanes $[Ti(RSiO_3)(OR')]_4$ (R′ = *t*Bu, O*t*Bu, CH$_2$*t*Bu) were found to be effective catalysts for the epoxidation of olefins by *tert*-butylhydroperoxide.[7b] Recently, we have explored the $(CuMes)_4$ copper species to get insight into the importance of silica-supported copper-containing catalysts. A large cage compound $[RSi(OCu)_3]_8$[7c] was successfully isolated from the reaction of the organocopper(I) $(CuMes)_4$ (Mes = 2,4,6-$Me_3C_6H_2$) with the N-bonded silanetriol $RSi(OH)_3$ (R = $N(SiMe_3)Ar$, Ar = 2,6-$i Pr_2C_6H_3$).[8] This complex features a 56-membered SiOCu core constructed by basic building blocks of six Cu_4O_4 squares and 12 $Cu_2Si_2O_4$ hexagons. Encouraged by this finding, we continued to investigate the reactions of $(CuMes)_4$ with the β-diketiminato ligand-stabilized methylaluminum monohydroxide LAlMe(OH) (L = $HC[C(Me)N(Ar)]_2$, β-diketiminato ligand). The latter has been recognized to be a useful precursor to develop well-defined heterobimetallic compounds bearing AlMe(μ-O)Zr,[6a] and AlMe(μ-O)Ln linkages.[6b] On the basis of these results, we prepared a series of organoaluminum hydroxides LAlR(OH) supported by β-diketiminato ligand with a variety of substituents on aluminum (R = Me, Et, Ph, OEt, $OSiMe_3$).[6c,d] Their reactivity with Cp_2ZrMe_2 was examined to afford the corresponding heterobimetallic oxide LAlR(μ-O)$ZrMeCp_2$.[6c] Consequently,

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we became interested in studying the detailed reaction of $(CuMes)_4$ with the organoaluminum monohydroxide.

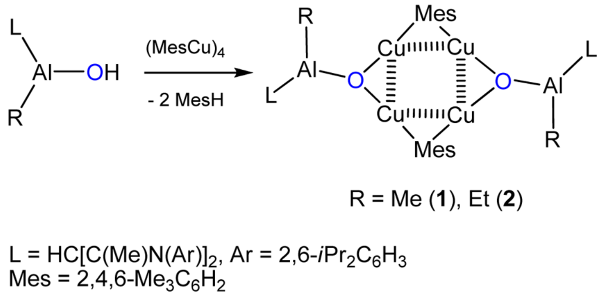
Furthermore, the organoaluminum dihydroxide $LAl(OH)_2$ has also been reported.[9a] However, its reactivity is quite unknown. In a previous contribution we described that treatment of $LAl(OH)_2$ with 1 equiv of $HAl(OAr^*)_2$ (Ar* = 4-Me-2,6-tBu$_2$C$_6$H$_2$) resulted in the isolation of LAl(OH)(μ-O)Al(OAr*)$_2$, with an intact OH group on the Al center.[9b] We were curious to know if both of the two hydroxyl protons could be reacted using $(CuMes)_4$ as the deprotonating agent.

Herein, we report on the synthesis, characterization, and structure of Cu(I) oxides containing the Al−O−Cu moiety by reacting $(CuMes)_4$ with the organoaluminum monohydroxides LAlR(OH) (L = HC[C(Me)N(Ar)]$_2$; R = Me, Et), and organoaluminum dihydroxide $LAl(OH)_2$.

2. RESULTS AND DISCUSSION

Treatment of $(CuMes)_4$ with organoaluminum monohydroxide LAlMe(OH) (L = HC[C(Me)N(Ar)]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) in a 1:2 molar ratio gave an isolable product as colorless crystals in moderate yield (**1**, Scheme 1). In the ^{1}H NMR spectrum of **1** the pattern is recognized as the characteristic resonances for the backbone of the β-diketiminato ligand. The high-field singlet (−0.62 ppm) is assigned for the methyl group of Al*Me*, while the disappearance of the O*H* proton resonance indicates the intermolecular elimination of MesH. Two additional singlets (2.23, 2.58 ppm) are due to the methyl protons of the Mes groups, suggesting a chemical composition of **1** as [LAl(Me)-OCu·MesCu]$_2$ (Scheme 1).

Scheme 1. Preparation of Compounds 1 and 2



The structure of [LAl(Me)OCu·MesCu]$_2$ (**1**) was further confirmed by X-ray single-crystal diffraction (Figure 1). Compound **1** crystallizes in the monoclinic space group $P2_1/n$, and exhibits the quasisquare $Cu_4O_2C_2$ and the *trans* arrangement of LAlMe fragments relative to the $Cu_4O_2C_2$ core.

Likewise, **1** can be seen as a self-assembly of two L(R)AlOCuMes cuprate-type anions and two Cu cations,[10] or alternatively of two LAl(Me)OCu and two MesCu fragments to form a heterobimetallic tetranuclear Cu(I) methylalumoxane. The Cu−O (1.855(1), 1.865(1) Å) and Al−O (1.710(7) Å) bond lengths are evidently shorter than those in the alkoxide adduct [Cu·Al(OtBu)$_4$]$_2$ (av 1.886 Å for Cu−O and 1.801 Å for endocyclic Al−O bonds).[11]

We reasoned that the ethyl-substituted organoaluminum monohydroxide LAlEt(OH) might have an influence on the product formation with $(CuMes)_4$ (Scheme 1). The isolated product turned out to be [LAl(Et)OCu·MesCu]$_2$ (**2**). In the ^{1}H NMR spectrum the two singlets are assigned to the methyl proton resonances of the Mes groups (2.20 and 2.62 ppm with an integrated ratio of 1:2). Compound **2** crystallizes in the triclinic space group $P\bar{1}$. Its molecular structure (Figure S1, see Supporting Information) is analogous to that of **1**. This is not surprising, since the ethyl substituent shows only small differences as compared to its methyl counterpart. However, the β-diketiminato ligand-supported aluminum monohydroxide LAl(Et)(OH) proves to be a reactive precursor to form heterobimetallic oxide systems. In compound **1** the copper−copper distances bridged by the Mes group have a slightly longer bond length (2.4158(1) Å) when compared with those (2.393(16), 2.395(16) Å) in **2**, whereas the O-linked copper−copper separations are shorter (2.6221(2) Å) in **1**, than those in **2** (2.729(17) Å).

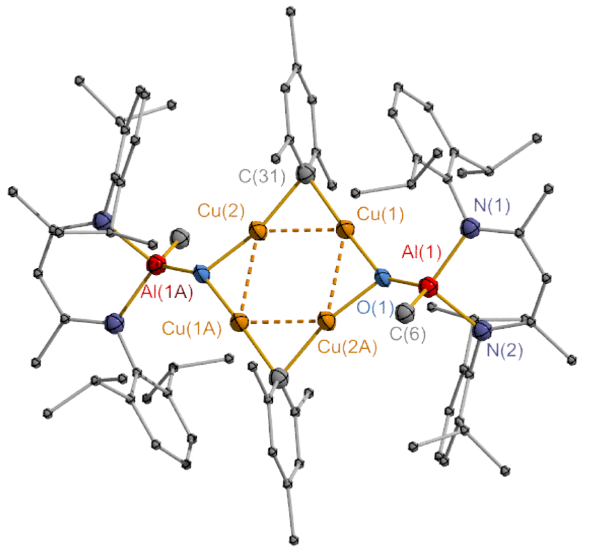


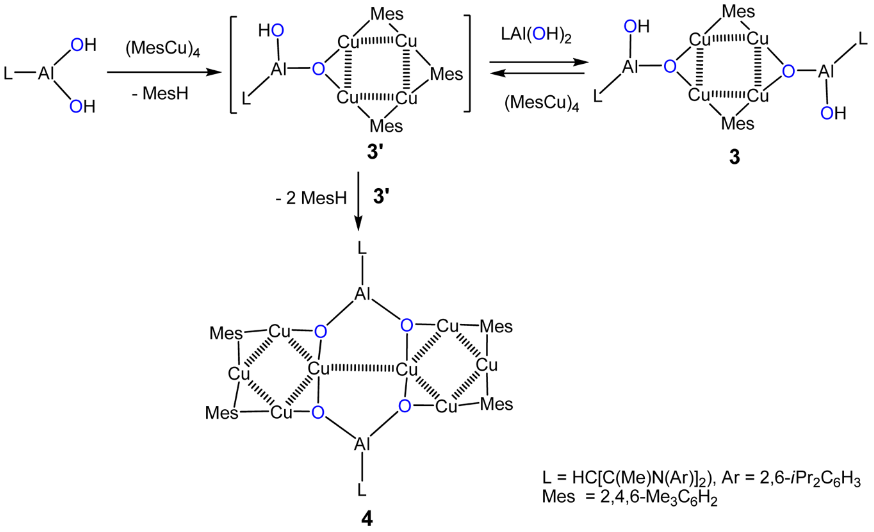
Figure 1. Molecular structure of [LAl(Me)OCu·MesCu]$_2$ (**1**). Thermal ellipsoids are drawn at 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths/Å and angles/deg: Cu(1)···Cu(2) 2.415(8), Cu(1)···Cu(2A) 2.622(1), Cu(1)−O(1) 1.855(1), Cu(2)−O(1) 1.865(1), Al(1)−O(1) 1.710(7), Al(1)−C(6) 1.967(1); Cu(1)−O(1)−Cu(2) 89.62(11).

Structurally investigated compounds bearing the Al−O−Cu linkage have been reported. Most of them are prepared from the reaction of aluminum- with copper-alkoxides (or silanolates) under formation of AlO_2Cu four-membered rings.[11,12] Compound [LAl(R)OCu·MesCu]$_2$ (R = Me, **1**; Et, **2**) represents a rare example containing the Al−O−Cu linkage where all aluminum atoms are in exocyclic positions of the ring skeleton.

We were not successful in eliminating the Mes groups in [LAl(R)OCu·MesCu]$_2$ (R = Me, **1**; Et, **2**) by using additional LAl(R)(OH) or isolating the LAl(R)OCu fragment in the presence of NHC (N-heterocyclic carbene).[13] Previously, we reported a few examples using LAl(R)OH to yield the heterobimetallic Al−O−M (M = Zr, Hf, Ln) compounds containing the two-coordinate oxygen bridge and the bulky group (i.e., Cp) at the M.[6] In LAl(R)OCu the copper is less protected and has a tendency to bind MesCu to form **1** (or **2**), as a product. However, [LAl(R)O]$_2$(μ-Cu)$_2$ was actually not obtained, probably due to the geometry requirement for the two-coordinate Cu(I) center. The Cu$_4$ unit was rigidly retained in **1**, **2**, [RSi(OCu)$_3$]$_8$,[7c] and (Ph$_3$SiOCu)$_4$.[14]

Furthermore, we tried to treat $(CuMes)_4$ with an organoaluminum dihydroxide $LAl(OH)_2$. When the reaction was carried out in a 1:4 molar ratio from low temperature to room temperature, the purified product was the dimeric [LAl(OH)-

Scheme 2. Preparation of Compounds 3 and 4



L = HC[C(Me)N(Ar)]$_2$), Ar = 2,6-*i*Pr$_2$C$_6$H$_3$
Mes = 2,4,6-Me$_3$C$_6$H$_2$

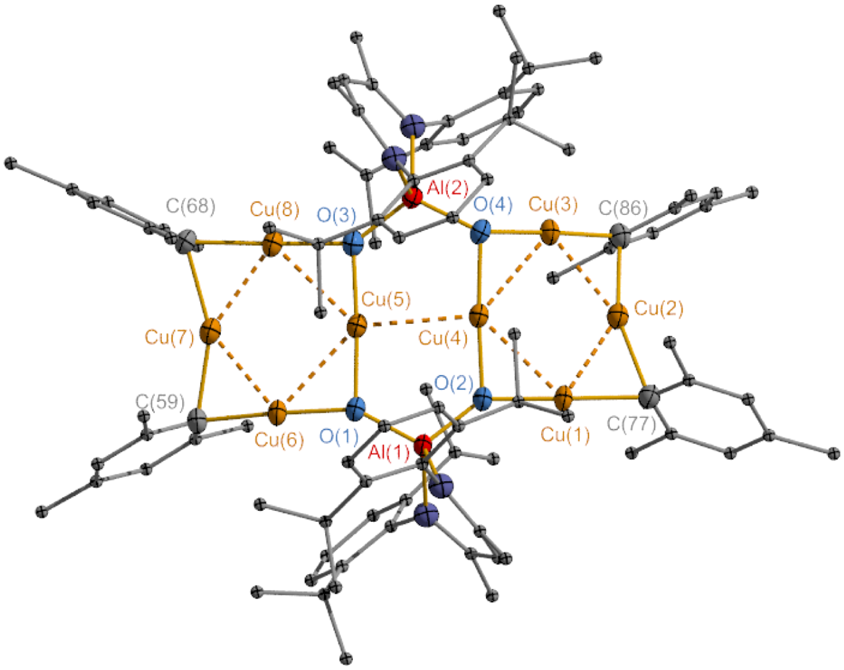


Figure 2. Molecular structure of [LAl(OCu·MesCu)$_2$]$_2$ (**4**). Thermal ellipsoids are drawn at 50% level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths/Å and angles/deg: Cu(1)···Cu(2) 2.394(3), Cu(2)···Cu(3) 2.418(0), Cu(6)···Cu(7) 2.423(9), Cu(7)···Cu(8) 2.398(1), Cu(1)···Cu(4) 2.651(7), Cu(3)···Cu(4) 2.636(5), Cu(5)···Cu(6) 2.635(9), Cu(5)···Cu(8) 2.694(2), Cu(4)···Cu(5) 2.754(1), Cu(1)−O(2) 1.835(2), Cu(3)−O(4) 1.854(2), Cu(4)−O(2) 1.846(2), Cu(4)−O(4) 1.854(2), Cu(5)−O(3) 1.850(2), Cu(5)−O(1) 1.868(2), Cu(6)−O(1) 1.843(2), Cu(8)−O(3) 1.840(2), Al(1)−O(1) 1.709(2), Al(1)−O(2) 1.714(2), Al(2)−O(4) 1.711(2), Al(2)−O(3) 1.719(2); Cu(6)−O(1)−Cu(5) 90.49(10), Cu(1)−O(2)−Cu(4) 92.18(10), Cu(8)−O(3)−Cu(5) 93.81(10), Cu(3)−O(4)−Cu(4) 90.62(10), O(1)−Cu(5)−O(3) 176.18(10), O(2)−Cu(4)−O(4) 176.04(10).

OCu·MesCu]$_2$ (**3**, Scheme 2). In the ^{1}H NMR spectrum, the chemical shift of the AlO*H* proton resonance is observed at 0.45 ppm as a singlet, which is further supported by the presence of a sharp absorption at 3728 cm^{-1} in the FT-IR spectrum for the OH stretching vibration. The methyl protons of the Mes groups resonate at 2.30 and 2.34 ppm, respectively. The single-crystal X-ray molecular structure of **3** is depicted in Supporting Information Figure S2, which is exactly analogous to that of [LAl(R)OCu·MesCu]$_2$ (R = Me, **1**; Et, **2**). It can be noticed that an unreacted hydroxyl group is present on each Al center. This is comparable with the results found for the reaction of LAl(OH)$_2$ with HAl(OAr*)$_2$.[9b]

In a parallel experiment, the same reaction mixture as that for the preparation of **3** was slowly heated and kept at 70 °C to allow the isolation of product **4** (Scheme 2).

The ^{1}H NMR spectrum of **4** showed the absence of the OH resonance which was found either in the parent LAl(OH)$_2$ or in [LAl(OH)OCu·MesCu]$_2$ (**3**), indicating the complete deprotonation of both hydroxyl protons of the AlOH groups. The methyl protons of *p*-Me (1.81, 2.05 ppm) and *o*-Me (2.51, 2.90 ppm) of Mes groups each resonate at two different chemical shifts with equal integration. The X-ray single-crystal analysis reveals the molecular structure of $[LAl(OCu{\cdot}MesCu)_2]_2$ (**4**) as a dimeric octanuclear Cu(I) compound in the triclinic space group $P\bar{1}$ (Figure 2). One toluene and two *n*-hexane (with some degree of disorder) solvent molecules cocrystallized in the unit cell and are deleted in Figure 2.

The two O−Cu−O units in **4** are almost linear (176.18(10)°, 176.04(10)°), which indicates the formation of a hexagonal central $Cu_2Al_2O_4$ ring of the core structure. Each elongated side of the $Cu_2O_4Al_2$ hexagon is connected to an edge sharing $Cu_4O_2C_2$ square. In view of the shape and functionality, these two kinds of eight-membered rings ($C_2Cu_4O_2$ square and $Cu_2Al_2O_4$ hexagon) are essentially the same as those found in $[RSi(OCu)_3]_8$.[7c] The difference between compounds **1**−**3** and **4** is that in the latter two residual Mes groups in each $C_2Cu_4O_2$ square take place at the neighboring (not diagonal) position. All oxygen atoms in **4** are three-coordinate, and each binds to one aluminum and two copper atoms, yet they are similar to those related in **1**−**3**. However, in compound **4** the two-coordinate copper atoms are involved in O−Cu−O, O−Cu−C, and C−Cu−C bonding patterns, respectively. The Cu−O bond lengths (1.835(2)−1.868(2) Å) and the O−Cu−O bond angles (176.04(10)−176.18(10)°) are close to those for $(Ph_3SiOCu)_4$ (1.833(4)−1.856(4) Å; 175.35(17)−176.32(17)°),[14] $[Ph(OtBu)_2SiOCu]_4$ (1.827(5)−1.844(4) Å; 174.1(2)−174.3(2)°),[15] and $[RSi(OCu)_3]_8$ (1.831(4)−1.865(3) Å; 174.53(14)−177.49(14)°).[7c] The Cu···Cu distances in $Cu_4O_2C_2$ squares (2.394(3)−2.423(9) Å for Mes-bridged couples and 2.635(9)−2.694(2) Å for O-bridged couples) and in the $Cu_2O_4Al_2$ hexagon (2.754(1) Å) are in the normal range.[16]

In an alternative route $[LAl(OCu{\cdot}MesCu)_2]_2$ (**4**) can be obtained by the subsequent treatment of $[LAl(OH)OCu{\cdot}MesCu]_2$ (**3**) with 1 equiv of $(CuMes)_4$. However, this reaction process is somewhat complicated, due to the fact that we were not able to isolate the product containing the Mes groups in the diagonal position. The reaction in a sealed NMR tube of $LAl(OH)_2$ with $(CuMes)_4$ in a 1:1 molar ratio was monitored for 48 h by ^1H NMR spectroscopy in C_6D_6 at ambient temperature (Supporting Information Figure S4). Within the first 4 h an intermediate **3′** was dominantly formed as indicated by the characteristic chemical shifts of protons of *γ-CH* (4.87 ppm) and Al*OH* (0.69 ppm), respectively. The latter resonance was found to be much closer to that of the monomeric $LAl(OH)(\mu\text{-}O)Al(Ar^*)_2$ (0.61 ppm).[9b] Combined with the NMR integration analysis, the intermediate **3′** was suggested with the composition of $LAl(OH)OCu{\cdot}(MesCu)_3$ (Scheme 2). With the progress of the NMR-tube reaction, it was noticed that **3′** is able to consume the residual $LAl(OH)_2$ to increase the amount of $[LAl(OH)OCu{\cdot}MesCu]_2$ (**3**). Moreover, **3** can redistribute with additional $(MesCu)_4$ to produce **3′** and vice versa (Supporting Information Figure S5). Finally, the NMR-tube reaction produced **4** as the end product. It is therefore suggested that two molecules of **3′** can undergo intramolecular elimination of MesH leading to the formation of **4** (Scheme 2). Both $LAl(OH)OCu{\cdot}(MesCu)_3$ (**3′**) and $[LAl(OCu{\cdot}MesCu)_2]_2$ (**4**) are the products of the 1:1 reaction of $LAl(OH)_2$ with $(CuMes)_4$. However, the intermediate **3′** could not successfully be obtained as a stable isolated product.

Compound **4** is the first product of the $LAl(OH)_2$ precursor with the double deprotonation of the hydroxyl groups, which shows a quite different structure when compared with its sulfur congener $[LAl(SCu)_2]_2$.[17] On one hand, it proves that organoaluminum dihydroxide $LAl(OH)_2$ is essentially a reactive and useful precursor for the production of soluble heterobimetallic oxides. On the other hand, compound **4** itself can be used as an interesting precursor to evoke further reactions. Attempts to trigger the tandem reaction of **4** with $LAl(OH)_2$ were not successful. However, it still can be reasonably expected, in an extensive scope, that a less bulky L′ ligand or a more reactive RM(I) system could fulfill the complete deprotonation of $L'Al(OH)_2$ to give $[L'Al(OM)_2]_n$.

3. CONCLUSION

Reactions of $(CuMes)_4$ with the functionalized OH group at the aluminum of LAl(R)OH (L = $HC[C(Me)N(Ar)]_2$; Ar = 2,6-$i$$Pr_2C_6H_3$; R = Me, Et) have been shown to be thermodynamically favorable to synthesize dimeric Cu(I) complexes containing the Al−OCu·MesCu unit (**1**−**2**). However, the residual Mes groups could not be eliminated by the excess addition of hydroxyl precursor. These compounds are structurally analogous to each other, in terms of the $(OCu{\cdot}MesCu)_2$ core and diagonal position of the Mes groups as well as the *trans* arrangement of peripheral functionalities. Similarly, the reaction of the aluminum dihydroxide $LAl(OH)_2$ in a 1:2 ratio gave the same derivative (**3**) with the $(OCu{\cdot}MesCu)_2$ core and one unreacted OH group on each Al center. When a 1:1 mixture of $(CuMes)_4$ and $LAl(OH)_2$ was treated at elevated temperature, the dimeric adduct **4** was formed, which contains two $(OCu{\cdot}MesCu)_2$ units joined by two Al centers. One structural feature of **4** is distinguished from those of **1**−**3** in that the two Mes groups in each $(OCu{\cdot}MesCu)_2$ unit are located at the neighboring position. Compound **4** adopts a similar self-assembly when compared to the organosilanetriol and -silanediol derivatives, and shows an interesting challenge to the potential assembling of Al−O−Cu prisms with sizable cavities.

■ EXPERIMENTAL SECTION

All manipulations were carried out under a dry argon or nitrogen atmosphere using Schlenk line and glovebox techniques. Solvents including toluene, *n*-hexane, and tetrahydrofuran were dried by refluxing with sodium/potassium benzophenone under N_2 prior to use. The NMR (^1H and ^{13}C) spectra were recorded on a Bruker Avance II 400 or 500 MHz spectrometer. Infrared spectra were obtained on a Nicolet FT-IR 330 spectrometer. Melting points of compounds were measured in a sealed glass tube using the Büchi-540 instrument. Elemental analysis was performed with a Thermo Quest Italia SPA EA 1110 instrument. Commercial reagents were purchased from Aldrich, Acros, or Alfa-Aesar Chemical Co. and used as received. Compounds LAlMe(OH) (L = $HC[C(Me)N(Ar)]_2$), LAlEt(OH), $LAl(OH)_2$,[6c,d,8,9a] $(CuMes)_4$,[18] and NHC[13] were prepared according to literature.

$[LAl(Me)OCu{\cdot}MesCu]_2$ (1). LAl(Me)OH (0.238 g, 0.5 mmol) and $(CuMes)_4$ (0.183 g, 0.25 mmol) were added to a flask. Cold toluene (15 mL) was added drop by drop into the flask under stirring at −20 °C. The mixture was warmed to room temperature and stirred for an additional 12 h. Then, the solvent was removed under vacuum to give an oil. *n*-Hexane (15 mL) was added to the flask. After filtration, the filtrate was kept at 4 °C. One week later, colorless crystals were yielded and collected by filtration (0.21 g, 58%). Mp: 270 °C. ^1H NMR (500 MHz, C_6D_6, 298 K, ppm): $\delta = -0.62$ (s, 3 H, Al*Me*), 1.08 (d, 6 H, $^3J_{HH} = 6.5$ Hz, CH*Me*$_2$), 1.21 (d, 6 H, $^3J_{HH} = 7.0$ Hz, CH*Me*$_2$), 1.22 (d, 6 H, $^3J_{HH} = 6.5$ Hz, CH*Me*$_2$), 1.47 (s, 6 H, *β-Me*), 1.52 (d, 6 H, $^3J_{HH} =$ 7.0 Hz, CH*Me*$_2$), 2.23 (s, 3 H, *p-Me*), 2.58 (s, 6 H, *o-Me*), 3.15 (sept, 2 H, $^3J_{HH} = 7.0$ Hz, C*H*Me$_2$), 3.62 (sept, 2 H, $^3J_{HH} = 7.0$ Hz, C*H*Me$_2$), 4.67 (s, 1 H, *γ-CH*), 6.66 (s, 2 H, C_6H_2), 6.97−7.04 (m, 6 H, C_6H_3). ^{13}C NMR (125 MHz, C_6D_6, 298 K, ppm): $\delta = 14.31$ (Al*Me*), 21.60, 23.42, 24.78, 24.86, 25.75, 26.49, 28.05, 28.70, 30.40 (*o-Me*, *p-Me*, CH*Me*$_2$, C*Me*), 97.46 (γ-CH), 124.22, 124.27, 125.70, 128.35, 139.17, 140.94, 143.88, 144.45, 157.71 (C_6H_3, C_6H_2), 169.14 (CN). Anal. Calcd (%) for $C_{78}H_{110}Al_2Cu_4N_4O_2$ (M_r = 1443.88): C, 64.88; H, 7.68; N, 3.88. Found: C, 65.16; H, 7.37; N, 4.04.

[LAl(Et)OCu·MesCu]$_2$ (2). Preparation of **2** was accomplished like that of **1** from LAlEt(OH) (0.245 g, 0.5 mmol) and $(CuMes)_4$ (0.183 g, 0.25 mmol). X-ray quality crystals were grown from *n*-hexane (0.15 g, 41%). Mp: 287 °C. ^{1}H NM R (500 MHz, C_6D_6, 298 K, ppm): δ = −0.02 (br, 2 H, AlC*H*$_2$CH$_3$), 1.10 (br, 9 H, AlCH$_2$C*H*$_3$, CH*Me*$_2$), 1.27 (d, 12 H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 1.48 (s, 6 H, *β-Me*), 1.57 (d, 6 H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 2.20 (s, 3 H, *p-Me*), 2.62 (s, 6 H, *o-Me*), 3.23 (br, 2 H, C*H*Me$_2$), 3.65 (br, 2 H, C*H*Me$_2$), 4.62 (s, 1 H, *γ−CH*), 6.69 (s, 2 H, C$_6$*H*$_2$), 6.98−7.07 (m, 6 H, C$_6$*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6, 298 K, ppm): δ = 1.41, 9.78 (AlCH$_2$CH$_3$), 21.58, 23.41, 24.90, 24.91, 28.65, 30.61(*o-Me*, *p-Me*, C*Me*, CH*Me*$_2$), 97.90 (γ-CH), 124.16, 124.42, 125.68, 127.08, 128.35, 139.36, 141.14, 143.82, 157.69 (C_6H_3, C_6H_2), 169.52 (CN). Anal. Calcd (%) for $C_{80}H_{114}Al_2Cu_4N_4O_2$ (M_r = 1471.93): C, 65.28; H, 7.81; N, 3.81. Found: C, 65.61; H, 7.35; N, 3.92.

[LAl(OH)OCu·MesCu]$_2$ (3). Preparation of **3** was accomplished from LAl(OH)$_2$ (0.239 g, 0.5 mmol) and $(CuMes)_4$ (0.183 g, 0.25 mmol). A colorless crystal was yielded after 1 day at 4 °C (0.18 g, 50%). Mp: 285 °C (decomposed). ^{1}H NMR (500 MHz, C_6D_6, 298 K, ppm): δ = 0.45 (s, 1 H, AlO*H*), 1.01 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, CH*Me*$_2$), 1.14 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, CH*Me*$_2$), 1.31 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, CH*Me*$_2$), 1.45 (s, 6 H, *β-Me*), 2.30 (s, 6 H, *o-Me*), 2.34 (s, 3 H, *p-Me*), 3.14 (sept, $^3J_{HH}$ = 7.0 Hz, 2 H), 3.5 (sept, $^3J_{HH}$ = 7.0 Hz, 2 H) (C*H*Me$_2$), 4.79 (s, 1 H, *γ-CH*), 6.62 (s, 2 H, C$_6$*H*$_2$), 6.96−7.03 (m, 6 H, C$_6$*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6, 298 K, ppm): δ = 21.70, 23.17, 24.43, 24.71, 24.84, 25.94, 27.68, 28.69, 29.63 (*o-Me*, *p-Me*, C*Me*, CH*Me*$_2$), 96.85 (γ-CH), 123.75, 124.33, 125.65, 127.25, 138.97, 140.20, 143.39, 144.46, 157.61 (C_6H_3, C_6H_2), 169.85 (CN). IR (KBr plate, cm^{-1}): $\tilde{\nu}$ 3728 (O−H). Anal. Calcd (%) for $C_{76}H_{106}Al_2Cu_4N_4O_4$ (M_r = 1447.83): C, 63.05; H, 7.38; N, 3.87. Found: C, 63.26; H, 7.54; N, 3.96.

[LAl(OCu·MesCu)$_2$]$_2$ (4). LAl(OH)$_2$ (0.239 g, 0.5 mmol) and $(CuMes)_4$ (0.366 g, 0.5 mmol) were dissolved in toluene (20 mL). Then, the mixture was stirring overnight at 70 °C. The color changed from yellow-green to light yellow. After cooling to room temperature, the solvent was removed under vacuum, and *n*-hexane (30 mL) was added. After filtration, the filtrate was kept at 4 °C. After 24 h, colorless crystals were yielded and collected by filtration (0.29 g, 60%). Mp: 293 °C (decomposed). ^{1}H NMR (500 MHz, C_6D_6, 298 K, ppm): δ = 0.93 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, CH*Me*$_2$), 1.16 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, CH*Me*$_2$), 1.46 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, CH*Me*$_2$), 1.72 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, CH*Me*$_2$), 1.30 (s, 6 H, *β-Me*), 1.81 (s, 3 H, *p-Me*), 2.05 (s, 3 H, *p-Me*), 2.51 (s, 6 H, *o-Me*), 2.90 (s, 6 H, *o-Me*), 3.16 (sept, $^3J_{HH}$ = 7.0 Hz, 2 H, C*H*Me$_2$), 3.80 (sept, $^3J_{HH}$ = 7.0 Hz, 2 H, C*H*Me$_2$), 4.64 (s, 1 H, *γ-CH*), 6.62 (d, $^3J_{HH}$ = 7.0 Hz, 4 H, C$_6$*H*$_3$), 7.05 (m, 2 H), 7.32−7.37 (m, 4 H) (C$_6$*H*$_3$, C$_6$*H*$_2$). ^{13}C NMR (125 MHz, C_6D_6, 298 K, ppm): δ = 21.22, 21.47, 23.44, 24.55, 24.83, 24.87, 28.28, 28.38, 28.80, 29.69, 30.48 (*o-Me*, *p-Me*, C*Me*, CH*Me*$_2$), 97.72 (γ-CH), 124.20, 125.27, 125.90, 126.19, 126.93, 131.47, 132.11, 139.79, 139.96, 141.99, 143.70, 145.68, 155.32, 156.24 (C_6H_3, C_6H_2), 170.28 (CN). Anal. Calcd (%) for $C_{94}H_{126}Al_2Cu_8N_4O_4$, ($M_r$ = 1938.36): C, 58.25; H, 6.55; N, 2.89. Found: C, 57.82; H, 7.01; N, 2.92.

X-ray Crystallography. X-ray crystallographic data were collected at 173 K on an Oxford Gemini S Ultra system (Mo Kα radiation, λ = 0.710 73 Å for **1**−**3**; Cu Kα radiation, λ = 1.541 78 Å for **4**) with a ω−2θ scan technique. The structure was solved by direct methods with SHELX-97.[19] A full-matrix least-squares refinement on F^2 was carried out by using SHELXL-97.[20]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information files (CIFs) for compounds **1**−**4**, molecular structures for **2** (Figure S1) and **3** (Figure S2) alone with **4** in an overhead ORTEP-drawing view (Figure S3), structural data in Table S1 for **1**−**4**, and spectroscopic diagrams (Figures S4−S13). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00990.

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Notes

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