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Lithium Aluminates on a Molecular Titanium Oxide

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Supporting Information

ABSTRACT: Lithium aluminates Li[Al(O-2,6-$Me_2C_6H_3$)R'_3] (R′ = Et, Ph) react with the μ_3-alkylidyne oxoderivative ligands [{Ti(η^5-C_5Me_5)(μ-O)}$_3$(μ_3-CR)] [R = H (**1**), Me (**2**)] to afford the aluminum–lithium–titanium cubane complexes [{R'_3Al(μ-O-2,6-$Me_2C_6H_3$)-Li}(μ_3-O)$_3${Ti(η^5-C_5Me_5)}$_3$(μ_3-CR)] [R = H, R′ = Et (**5**), Ph (**7**); R = Me, R′ = Et (**6**), Ph (**8**)]. Complex **7** evolves with the formation of a lithium dicubane species and a Li{Al(μ-O-2,6-$Me_2C_6H_3$)Ph_3}$_2$] unit.

The chemistry of heterobimetallic compounds that contain alkali metals has attracted the interest of many research groups for the last 3 decades. Compounds containing a central metal (magnesium, zinc, or aluminum), an alkali metal such as lithium or sodium, and a variable number of ligands have received the general term of "ate" complexes.[1] These species have revealed a remarkable structural diversity and different reactivity patterns in comparison with the homometallic precursors.[2]

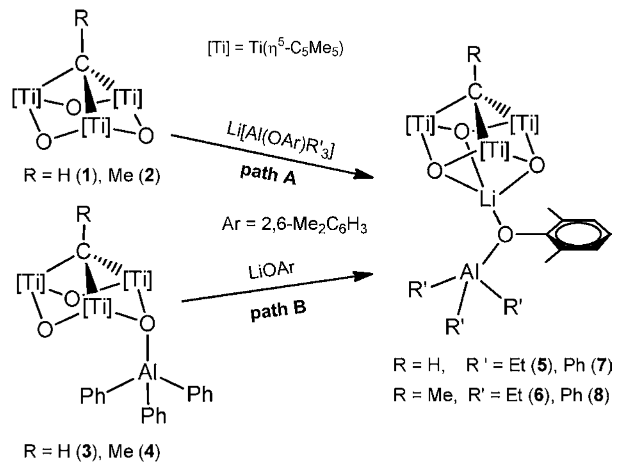
Recently, we have studied reactions of the μ_3-alkylidyne compounds [{Ti(η^5-C_5Me_5)(μ-O)}$_3$(μ_3-CR)] [R = H (**1**), Me (**2**)][3] with different group 13 homoleptic alkyl and halide derivatives and reported the formation of the corresponding adducts [{E_3M}(μ_3-O)(μ-O)$_2${Ti(η^5-C_5Me_5)}$_3$(μ_3-CR)] (R = H, Me; M = B, Al, Ga; E = alkyl, halide).[4] Surprisingly, analogous reactions with different lithium alkyl reagents led to coordination of the lithium atom through the three bridging oxygen atoms, dehydronation of the μ_3-CR apical moieties, and coupling of two formed units to give the dicubane complexes [Li(μ_4-O)(μ_3-O)$_2${Ti_3(η^5-C_5Me_5)$_3$(μ_3-X)}]$_2$ (X = C^-, CH_2^-).[5]

Now we are interested in studying the reactions of lithium aluminate derivatives with the mentioned μ_3-alkylidyne compounds. Herein we provide details about these reactions and illustrate the cocomplexation of the lithium aluminate moieties through different coordination modes in the solid-state structures.

The reaction of **1** and **2** and the aluminum "ate" compounds Li[Al(OAr)R'_3] (R′ = Et, Ph; Ar = 2,6-$Me_2C_6H_3$)[6] in hexane at room temperature allowed us to obtain the aluminum–lithium–titanium species [{R'_3Al(μ-OAr)Li}(μ_3-O)$_3${Ti(η^5-C_5Me_5)}$_3$(μ_3-CR)] [R = H, R′ = Et (**5**), Ph (**7**); R = Me, R′ = Et (**6**), Ph (**8**)],[7] as outlined in Scheme 1 (path A).

While complexes **5** and **6** were obtained with an acceptable purity by this method,[8] **7** and **8** contained some impurities. In fact, only when the adducts [{Ph_3Al}(μ_3-O)(μ-O)$_2${Ti(η^5-C_5Me_5)}$_3$(μ_3-CR)] [R = H (**3**), Me (**4**)][4b] were isolated and then treated with LiO-2,6-$Me_2C_6H_3$ were complexes **7** and **8** obtained in a pure form (Scheme 1, path B). In both synthetic protocols, after stirring, the resulting yellow (**5** and **7**) or red (**6** and **8**) microcrystalline solids were collected by filtration. The complexes, scarcely soluble in hexane but soluble in toluene, were characterized by analytical[8] and spectroscopic methods.

Scheme 1



The NMR spectra in benzene-d_6 of complexes **5**–**8** are in agreement with the structures depicted in Scheme 1. The single set of signals corresponding to the η^5-C_5Me_5 ligands is noteworthy, indicating a local C_{3v} symmetry for the μ_3-alkylidyne moieties. The AlR'_3 group and the O-2,6-$Me_2C_6H_3$ ligand show characteristic signals, and the μ_3-alkylidyne (μ_3-CR) unit exhibits resonances in the range found for species containing such moieties.[9,4b]

Crystals of **6** were grown from a toluene/hexane solution by cooling at −35 °C and crystallized with one molecule of toluene.[10] The molecular structure of **6** and selected distances and angles are given in Figure 1. The structure shows how the μ_3-alkylidyne metalloligand [{Ti(η^5-C_5Me_5)(μ-O)}$_3$(μ_3-CMe)] (**2**) stabilizes the lithium aluminate through tridentate coordination to the lithium atom, building a cube-type [LiTi_3O_3C] core with Li–O bond lengths in the range of 2.134(6)–2.273(6) Å. These distances are comparable to those found for [{Li(μ_4-O)(μ_3-O){Ti_3(η^5-C_5Me_5)$_3$(μ_3-C)}]$_2$ [2.03(1)–2.39(1) Å] if we take into account the difference between the tetrahedral environment of lithium in **6** and the trigonal pyramid in the dicubane species.[5a] The distance from the alkoxide atom O1 to Li1 [1.853(6) Å] is clearly shorter than those of the core but compares well with other lithium

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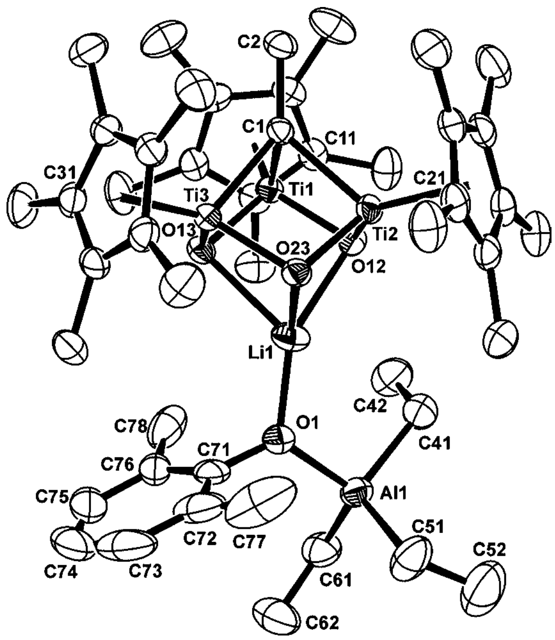
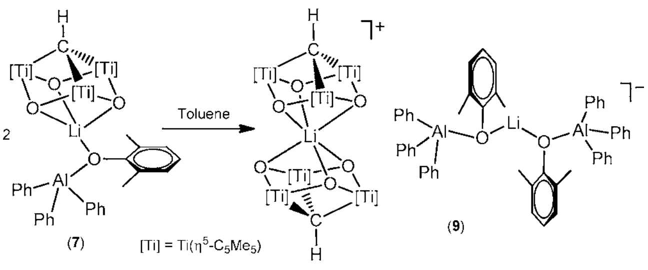


Figure 1. Crystal structure of complex **6**. Hydrogen atoms have been omitted for clarity. Average of selected lengths (Å) and angles (deg): C1−C2 1.518(4), Ti−C1 2.117(2), Al1−C 1.994(7), C71−O1 1.366(4), Al1−O1 1.861(2), Li1−O1 1.853(6), Li1−O23 2.134(6), Li1−O12 2.185(6), Li1−O13 2.273(6), Ti−O 1.853(4); Ti−C1−Ti 84.5(1), O1−Al1−C 101.2(1)−111.6(2), C−Al1−C 110.9(2), O1−Li1−O 122.9(3)−147.5(3), C71−O1−Li1 120.3(3), C71−O1−Al1 122.5(2), Li1−O1−Al1 116.9(2), Ti−O−Ti 100.4(4), Ti−O−Li1 89.4(2)−94.0(2), O−Ti−C1 87.2(3).

derivatives, containing bridging alkoxo groups, found in the literature.[11] The $[\mathrm{Li}\{\mu\text{-O(C71)}\}\mathrm{Al}]$ unit is planar, and the phenoxo ligand is almost perpendicular [83.7(1)°] to this plane. The C−Al [av. 1.994(7) Å] and Al1−O1 [1.861(2) Å] lengths are similar to those observed in other organoaluminium adducts.[12]

Whereas complexes **5**, **6**, and **8** are stable in benzene-d_6 solutions for long periods of time, the analogous compound **7** undergoes a chemical rearrangement to give complex **9**, which contains the lithium dicubane fragment $[\mathrm{Li}\{(\mu_3\text{-O})_3\mathrm{Ti}_3(\eta^5\text{-C}_5\mathrm{Me}_5)_3(\mu_3\text{-CH})\}_2]^+$ and the unprecedented lithium bis(aluminate) anion $[\mathrm{Li}\{(\mu\text{-O-Me}_2\mathrm{C}_6\mathrm{H}_3)\mathrm{AlPh}_3\}_2]^-$, as shown in Scheme 2. Compound **9** could be isolated in its pure form after several recrystallization steps in a two-pot reaction. First, the adduct complex $[\{\mathrm{Ph}_3\mathrm{Al}\}(\mu_3\text{-O})(\mu\text{-O})_2\{\mathrm{Ti}(\eta^5\text{-C}_5\mathrm{Me}_5)\}_3(\mu_3\text{-CH})]$ (**4**)[4b] reacts with LiO-2,6-$\mathrm{Me}_2\mathrm{C}_6\mathrm{H}_3$ in hexane to give **7**. Then, the isolated compound is dissolved in toluene and left to stir for 1 day to afford **9** as a light-orange microcrystalline solid in moderate yield.[13]

Scheme 2



The NMR spectra for complex **9** in benzene-d_6, consistent with the X-ray structural study,[10] reveal the presence of characteristic signals for μ_3-CH, phenyl, alkoxide, and η^5-$\mathrm{C}_5\mathrm{Me}_5$ groups.

Single crystals of **9** were formed by slow cooling at −35 °C in toluene after several weeks. The structure of the molecule, determined crystallographically (see Figure 2), confirms the existence of the corner-shared double cube $[\mathrm{LiTi}_6\mathrm{O}_6]$ unit and the lithium bis(aluminate) fragment shown in Scheme 2. The coordination geometry about Li1 is best described as trigonal antiprismatic, with O−Li−O angles spanning 75.9(2)−104.1(2)°. In this arrangement, the two trinuclear $[\mathrm{Ti}_3\mathrm{O}_3\mathrm{C}]$ units are situated in a relative alternate disposition because of hindrance of the pentamethylcyclopentadienyl groups. Bond lengths and angles within these units are very similar to those of the μ_3-alkylidyne starting materials.[3a]

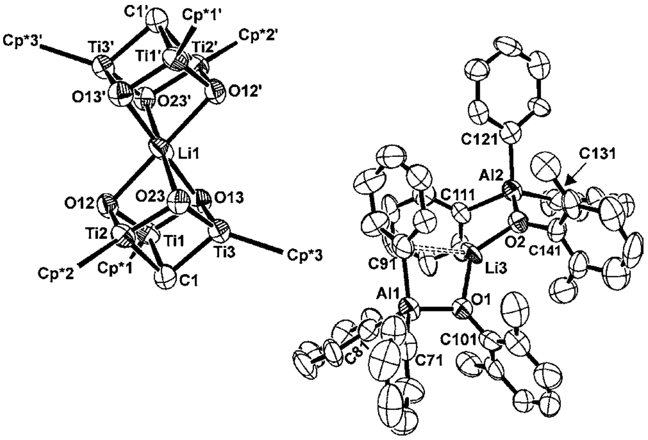


Figure 2. Crystal structure of complex **9**. Average of selected lengths (Å) and angles (deg): Ti−C1 2.056(8), Li1−O 2.23(4), Li1···Ti 2.94(1), Li3−O2 1.84(1), Li3−O1 1.87(1), Ti−O 1.841(9), Ti···Ti 2.82(1), Al1−O1 1.805(6), Al2−O2 1.807(6), Al1···Li3 2.91(1), Al2···Li3 3.01(1), Li3···C91 2.59(2); Ti−C1−Ti 86.7(2), O−Li1−O 75.9(2)−104.1(2), Ti−O−Ti 100.1(4), Ti−O−Li1 91.5(9), O−Ti−O 97.9(6), O−Ti−C1 86.3(3), O1−Li3−O2 133.7(8), Al1−O1−Li3 104.5(5), Al2−O2−Li3 111.3(5), O1−Al1−C 97.8(3)−111.9(3), O2−Al2−C 99.8(3)−113.5(3), C−Al1−C 107.6(4)−117.7(4), C−Al2−C 107.5(4)−113.7(4).

On the other hand, the anion presents the lithium atom linked to two aluminate units, with Li−O bond distances of 1.84(1) and 1.87(1) Å, similar to that found for complex **6**, and compares well to those reported for other lithium complexes with Li−O bonds,[14] but are slightly shorter than those found for the ion system $[(\mathrm{H}_5\mathrm{C}_2)\mathrm{Al}(\mathrm{OC}_6\mathrm{H}_5)_3{}^-\cdots\mathrm{Li}^+\cdots{}^-(\mathrm{H}_5\mathrm{C}_6\mathrm{O})_3\mathrm{Al}(\mathrm{C}_4\mathrm{H}_9)]^-$ published by Bock and co-workers.[15] However, if we take into account the short interaction Li3···C91 of 2.59(2) Å, the environment of this lithium atom should be considered as tricoordinate.[16] As shown in Figure 2, the aluminum atoms present a tetrahedral environment with Al−O bond lengths of ≈1.80 Å, slightly shorter than that of complex **6**. The low quality of the crystals precluded a deep study about possible weak interactions between the AlPh_3 phenyl rings.

In summary, the molecular organometallic oxide moiety $[\mathrm{Ti}_3\mathrm{O}_3\mathrm{C}]$ shows the capability of supporting heteroleptic aromatic lithium aluminum "ate" fragments. This process can be performed in two ways, by incorporation of the lithium aluminate fragment by coordination through the three oxygen atoms or by encapsulation of one lithium cation and simultaneous coordination of its aluminate moiety to other lithium aluminate units. Extension of these investigations is being actively developed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, full characterization data for **5**−**9**, and crystallographic data for **6** and **9** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) A hexane solution of AlR'_3 (R′ = Me, Et) at −35 °C was first treated with 1 mol equiv of a hexane solution of Li-O-2,6-$Me_2C_6H_3$ before stoichiometric amounts of **1** or **2** were introduced.

(7) There are two general methods to prepare compounds **5**−**8**. Method A: A solution of stoichiometric amounts of AlR'_3 (R′ = Et, Ph) in hexane (10 mL) at −35 °C was added to a solution of Li(O-2,6-$Me_2C_6H_3$) in hexane (10 mL) at −35 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Finally, complex **1** or **2** was added to the previous mixture and stirred. After 1 h (for **6** and **8**) or 1 night (for **5** and **7**), microcrystalline solids were observed at the bottom of the Schlenk flask. The solids were obtained by filtration and dried under a flux of argon. Method B: A suspension of adduct **3** or **4** and Li(O-2,6-$Me_2C_6H_3$) in hexane was stirred for 1 h. The new compounds were isolated by filtration and dried under a flux of argon. According to method A, **5** was obtained as a yellow microcrystalline solid from the reaction between $AlEt_3$ (0.34 g of a 1 M hexane solution, $\rho = 0.692$ g·mL^{-1}, 0.49 mmol), Li(O-2,6-$Me_2C_6H_3$) (0.063 g, 0.49 mmol), and **1** (0.30 g, 0.49 mmol). Yield: 0.20 g (48%). ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 13.07 (s, 1H, μ_3-*CH*), 7.06 (d, $^3J_{H-H} = 7.4$ Hz, 2H, *m*-O-2,6-$Me_2C_6\mathit{H}_3$), 6.82 (t, $^3J_{H-H} = 7.2$ Hz, 1H, *p*-O-2,6-$Me_2C_6\mathit{H}_3$), 2.56 (s, 6H, O-2,6-$\mathit{Me}_2C_6H_3$), 1.75 (s, 45H, $C_5\mathit{Me}_5$), 1.68 (t, $^3J_{H-H} = 8.2$ Hz, 9H, $AlCH_2\mathit{Me}$), 0.41 (q, $^3J_{H-H} = 8.2$ Hz, 6H, $Al\mathit{CH}_2Me$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 298 K): δ 402.5 (μ_3-CH), 157.5, 129.1, 128.7, 119.6 (O-2,6-$Me_2C_6H_3$), 123.1 (C_5Me_5), 18.5 (O-2,6-$\mathit{Me}_2C_6H_3$), 11.7 ($C_5\mathit{Me}_5$), 11.5 ($AlCH_2\mathit{Me}$), 3.0 ($AlCH_2Me$). Elem anal. Calcd for $C_{45}H_{70}AlLiO_4Ti_3$ (852.53): C, 63.40; H, 8.28. Found: C, 62.69; H, 8.00. The synthesis and characterization of complexes **6**−**8** can be found in the Supporting Information.

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(10) For further details about the X-ray studies, see the Supporting Information. CCDC 833161 (**6**) and 833162 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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(13) Synthesis of compound **9**: A total of 0.34 g of **7** was dissolved in toluene (20 mL), and the resulting solution was cooled at −35 °C for several weeks. A light-orange crystalline solid was isolated after the crystallization process. Yield: 0.12 g (35%). ^{1}H NMR (C_6D_6, 300 MHz, 333 K): δ 12.85 (s, 2H, μ_3-*CH*), 8.10−7.20 (30H, $Al\mathit{Ph}_3$), 7.00−6.70 (6H, O-2,6-$Me_2C_6H_3$), 2.38 (s, 12H, O-2,6-$\mathit{Me}_2C_6H_3$), 1.78 (s, 90H, $C_5\mathit{Me}_5$). Elem anal. Calcd for $C_{114}H_{140}Al_2Li_2O_8Ti_6$ (1993.31): C, 68.68; H, 7.08. Found: C, 68.67; H, 6.96.

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