Organometallics **1997,** *16,* 329−341

Structural Characterization of Dialkylaluminum Carboxylates: Models for Carboxylate Alumoxanes

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Received July 11, 1996⊗

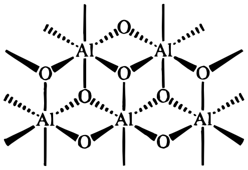
The reaction of $Al(^tBu)_3$ with carboxylic acids, RCO_2H, yields the dimeric di-*tert*-butylaluminum carboxylates $[(^tBu)_2Al(\mu\text{-}O_2CR)]_2$, where R = ^tBu (**1**), CCl_3 (**2**), Ph (**3**), CH_2Ph (**4**), $CHPh_2$ (**5**), CPh_3 (**6**), C(H)=C(H)Ph (**7**), CH_2OCH_3 (**8**), $CH_2OCH_2CH_2OCH_3$ (**9**), and $CH_2(OCH_2CH_2)_2OCH_3$ (**10**), which have been characterized by ^1H and ^{13}C NMR and IR spectroscopy and mass spectrometry. The molecular structures of compounds **1**, **3**, **4**, and **9** have been determined by X-ray crystallography, the first structural determinations for any such compounds. The carboxylate groups act as bidentate bridging ligands consistent with spectroscopic characterization. *Ab initio* calculations on the model compounds $H_2Al(\lambda^2\text{-}O_2CH)$, *eclipsed*-$H_2Al[OC(O)H]$, *staggered*-$H_2Al[OC(O)H]$, $[H_2Al(\mu\text{-}O_2CH)]_2$, and $[H_3Al\{OC(O)H\}]^-$ indicate that the observed carboxylate-bridged dimer is thermodynamically favored over the hypothetical chelating monomer. The $Al_2O_4C_2$ cyclic core in compound **1** is flat while those in compounds **3**, **4**, and **9** adopts chairlike conformations. The extent of the puckering of the core in $[(^tBu)_2Al(\mu\text{-}O_2CR)]_2$ is dependent on the steric bulk of the carboxylate substituent, R. The dimeric compounds, $[(^tBu)_2Al(\mu\text{-}O_2CR)]_2$, are satisfactory as simplistic structural models for the carboxylate groups bound to the boehmite-like core of carboxylate alumoxanes, $[Al(O)_x(OH)_y(O_2CR)_z]_n$, as prepared from the reaction of boehmite with a carboxylic acid. *Ab initio* calculations on the model anion $[(H_5Al)_2(\mu\text{-}O_2CH)]^{5-}$ indicate that the optimum Al···Al distance for the carboxylate ligand bridging two six-coordinate aluminum centers constrained on a surface is 3.2−3.8 Å. The carboxylate ligand is therefore near perfectly suited to bind to the (100) surface of boehmite, Al···Al = 3.70 Å, and hence stabilize the boehmite-like core in carboxylate alumoxanes.

Introduction

Recent work in our laboratory has focused on the synthesis of carboxylate alumoxanes[2] as precursors for $\gamma\text{-}Al_2O_3$[3] and aluminum-based mixed metal oxide ceramics.[4] Alumoxanes are traditionally formed by the hydrolysis of aluminum compounds or salts;[5,6] however, we have shown that in the case of carboxylate alumoxanes they may be more easily prepared by the reaction of the mineral boehmite with carboxylic acids, eq 1.[2,3]

$$[Al(O)(OH)]_n \xrightarrow{+HO_2CR\ (xs)} [Al(O)_x(OH)_y(O_2CR)_z]_n \quad (1)$$

The rational for this unusual synthetic methodology was that the aluminum−oxygen core of a hydrolytically stable alumoxane is structurally identical that of the mineral boehmite, *cf.*, **I**.[7,8]



(I)

The concept that molecular (or macromolecular) compounds may be prepared by the scission of a core fragment out of a continuous solid-state structure has been discussed,[9] and this reaction (eq 1) represents one of the simplest examples. However, the reason that carboxylic acids should be almost unique in their ability to react with boehmite to form alumoxanes is not clearly understood. In an effort to gain a greater understanding of this synthetic methodology we have undertaken an investigation of model compounds whose structures

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⊗ Abstract published in *Advance ACS Abstracts*, January 15, 1997.

[1] (a) Rice University. (b) Harvard University. (c) University of North Texas.

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[5] Alumoxanes formed from the hydrolysis of aluminum salts are commonly referred to as alumina gels or gelatinous alumina, see: Wefers, K.; Misra, C. *Oxides and Hydroxides of Aluminum*; Alcoa Laboratories: Alcoa, PA, 1987.

[6] See for example: (a) Andrianov, K. A.; Zhadanov, A. A. *J. Polym. Sci.* **1958**, *30*, 513. (b) Kimura, Y.; Tanimoto, S.; Yamane, H.; Kitao, T. *Polyhedron* **1990**, *9*, 371 and references therein.

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[8] It should be noted that the hydrolytically sensitive alkyl alumoxanes $[(R)Al(\mu_3\text{-}O)]_n$, prepared by the partial hydrolysis of aluminum alkyls, AlR_3, have cage structures: Barron, A. R. *Macromol. Symp.* **1995**, *97*, 15.

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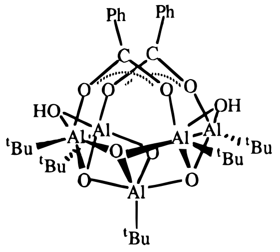
S0276-7333(96)00576-6 CCC: $14.00

reproduce the salient bonding features of the carboxylate alumoxanes.[10]

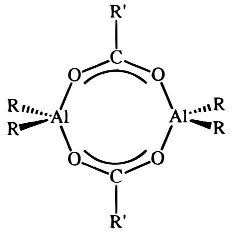
We have recently synthesized the pentaaluminum cage compound [$Al_5(^tBu)_5(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CPh)_2$] (**II**),[11]



(II)

whose structure is an excellent structural model of carboxylic bonding to a boehmite-like surface, since the Al_5 fragment resembles the (100) surface of boehmite. Unfortunately the very low yield, and difficulty in isolation, of this pentaaluminum compound render it impractical as a useful model for comparative studies, in particular where X-ray structural determinations are of prime importance. Thus, we have investigated simpler compounds to serve as convenient structural models.

Dialkyaluminum carboxylates, [$R_2Al(\mu\text{-}O_2CR')$]$_2$, represent the simplest isolable model compounds. They have been reported as the major products from the reaction of trialkylaluminum with carboxylic acids,[12] allowing for the isolation of the aluminum−methyl,[13] −ethyl,[14]−isobutyl,[15] and −phenyl[16] compounds. With utilization of IR and Raman spectroscopy, mass spectrometry, and molecular weight measurements, it has been proposed that the dialkylaluminum carboxylates are dimers which consist of an eight-membered ring with bridging carboxylates, i.e., **III**. Despite the apparent simplicity of these compounds, to date there has been no structural characterization of a dialkylaluminum carboxylate to confirm this structural motif. While this is surprising considering their comparative simplicity, it should be noted that the majority of examples previously reported are liquids (or oils) at room temperature.



(III)

Table 1. Selected Bond Lengths (Å) and Angles (deg) in [$(^tBu)_2Al(\mu\text{-}O_2C^tBu)$]$_2$ (1)

Al(1)−O(1)	1.809(3)	Al(1)−C(11)	1.960(6)
O(1)−C(1)	1.235(4)	C(1)−C(2)	1.517(7)
O(1)−Al(1)−O(1a)	107.6(1)	O(1)−Al(1)−C(11)	105.9(2)
O(1)−Al(1)−C(11a)	106.2(1)	C(11)−Al(1)−C(11a)	124.1(2)
Al(1)−O(1)−C(1)	155.1(3)	O(1)−C(1)−O(1a)	122.1(4)

Table 2. Selected Bond Lengths (Å) and Angles (deg) in [$(^tBu)_2Al(\mu\text{-}O_2CPh)$]$_2$ (3)

Al(1)−O(1)	1.809(3)	Al(1)−O(2)	1.811(3)
Al(1)−C(11)	1.965(5)	Al(1)−C(21)	1.960(5)
O(1)−C(1)	1.259(5)	O(2)−C(1)	1.254(4)
O(1)−Al(1)−O(2)	107.8(1)	O(1)−Al(1)−C(11)	106.7(2)
O(1)−Al(1)−C(21)	105.4(1)	O(2)−Al(1)−C(11)	106.8(2)
O(2)−Al(1)−C(21)	105.1(2)	C(11)−Al(1)−C(21)	124.2(2)
Al(1)−O(1)−C(1)	148.3(2)	Al(1a)−O(2)−C(1)	147.5(3)
O(1)−C(1)−O(2)	122.7(3)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) in [$(^tBu)_2Al(\mu\text{-}O_2CCH_2Ph)$]$_2$ (4)

Al(1)−O(1)	1.810(4)	Al(1)−O(2)	1.806(4)
Al(1)−C(11)	1.975(8)	Al(1)−C(21)	1.945(5)
O(1)−C(1)	1.224(5)	O(2)−C(1)	1.250(5)
C(1)−C(2)	1.473(6)	C(2)−C(3)	1.495(6)
O(1)−Al(1)−O(2)	106.5(2)	O(1)−Al(1)−C(11)	105.7(2)
O(1)−Al(1)−C(21)	105.0(2)	O(2)−Al(1)−C(11)	106.5(2)
O(2)−Al(1)−C(21)	106.6(2)	C(11)−Al(1)−C(21)	125.3(3)
Al(1)−O(1)−C(1)	151.5(3)	Al(1a)−O(2)−C(1)	150.2(3)
O(1)−C(1)−O(2)	123.4(4)	O(1)−C(1)−C(2)	117.9(5)
O(2)−C(1)−C(2)	118.7(5)	C(1)−C(2)−C(3)	116.3(5)

The lack of structural data for these alkylaluminum carboxylates, and their potential application as model compounds for carboxylate alumoxanes, [$Al(O)_x(OH)_y(O_2CR)_z$]$_n$, prompted our X-ray crystallographic investigation of this well-studied class of compounds.

Results and Discussion

Synthesis and Characterization of Di-*tert*-butylaluminum Carboxylates. The reaction of $Al(^tBu)_3$ with 1 molar equiv of the carboxylic acids RCO_2H yields the di-*tert*-butylaluminum carboxylates [$(^tBu)_2Al(\mu\text{-}O_2CR)$]$_2$, eq 2. The molecular structures of [$(^tBu)_2Al(\mu\text{-}O_2C^tBu)$]$_2$ (**1**), [$(^tBu)_2Al(\mu\text{-}O_2CPh)$]$_2$ (**3**), [$(^tBu)_2Al(\mu\text{-}O_2CCH_2Ph)$]$_2$ (**4**), and [$(^tBu)_2Al(\mu\text{-}O_2CCH_2OCH_2CH_2OCH_3)$]$_2$ (**9**) have been determined by X-ray crystallography; selected bond lengths and angles are given in Tables 1−4. To the best of our knowledge, these are the first structural characterizations reported for a dialkylaluminum carboxylate.

$$Al(^tBu)_3 + RCO_2H \rightarrow {}^1/_2[(^tBu)_2Al(\mu\text{-}O_2CR)]_2 + {}^tBuH \qquad (2)$$

$$\begin{aligned} R = {}^tBu\ (\mathbf{1}),\ CCl_3\ (\mathbf{2}),\ Ph\ (\mathbf{3}),\ CH_2Ph\ (\mathbf{4}),\\ CHPh_2\ (\mathbf{5}),\ CPh_3\ (\mathbf{6}),\ C(H){=}C(H)Ph\ (\mathbf{7}),\\ CH_2OCH_3\ (\mathbf{8}),\ CH_2OCH_2CH_2OCH_3\ (\mathbf{9}),\\ CH_2(OCH_2CH_2)_2OCH_3\ (\mathbf{10}) \end{aligned}$$

The structures of compounds **1**, **3**, **4**, and **9** consist of centrosymmetric dimers of two $(^tBu)_2Al$ units bridged by two carboxylate groups, as indicated in Figures 1−4.

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[10] This method is often termed the "synthetic analog approach"; see: Ibers, J. A.; Holm, R. H. *Science* **1988**, *209*, 223.

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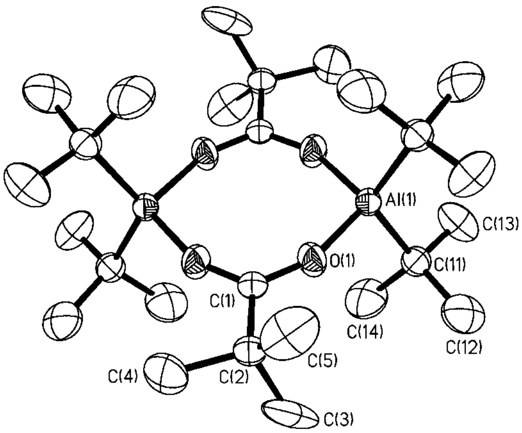

Figure 1. Molecular structure of $[(^tBu)_2Al(\mu\text{-}O_2C^tBu)]_2$ (**1**). Thermal ellipsoids are shown at the 30% level, and hydrogen atoms are omitted for clarity.

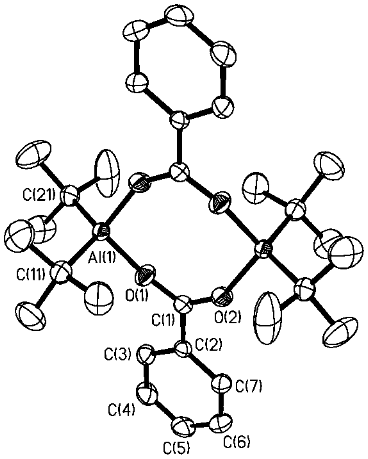

Figure 2. Molecular structure of $[(^tBu)_2Al(\mu\text{-}O_2CPh)]_2$ (**3**). Thermal ellipsoids are shown at the 30% level, and hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for the Two Crystallographically Independent Molecules of $[(^tBu)_2Al(\mu\text{-}O_2CCH_2OCH_2CH_2OCH_3)]_2$ (9)

molecule 1		molecule 2	
Al(1)−O(11)	1.806(6)	Al(2)−O(21)	1.767(7)
Al(1)−O(12)	1.837(6)	Al(2)−O(22)	1.836(8)
Al(1)−C(111)	2.00(1)	Al(2)−C(211)	1.94(1)
Al(1)−C(115)	1.93(1)	Al(2)−C(215)	2.00(1)
O(11)−C(11)	1.23(1)	O(21)−C(21)	1.25(1)
O(12)−C(11a)	1.24(1)	O(22)−C(21a)	1.25(1)
C(11)−C(12)	1.52(1)	C(21)−C(22)	1.46(1)
O(11)−Al(1)−O(12)	103.1(3)	O(21)−Al(2)−O(22)	105.5(3)
O(11)−Al(1)−C(111)	106.9(4)	O(21)−Al(2)−C(211)	107.2(4)
O(11)−Al(1)−C(115)	107.3(4)	O(21)−Al(2)−C(215)	105.9(5)
O(12)−Al(1)−C(111)	107.0(4)	O(22)−Al(2)−C(211)	104.6(5)
O(12)−Al(1)−C(115)	105.4(4)	O(22)−Al(2)−C(215)	104.8(4)
C(111)−Al(1)−C(115)	125.2(4)	C(11)−Al(2)−C(215)	127.1(6)
Al(1)−O(11)−C(11)	157.6(7)	Al(2)−O(21)−C(21)	172.8(7)
Al(1)−O(12)−C(11a)	134.9(4)	Al(2)−O(22)−C(21a)	137.3(4)
O(11)−C(11)−O(12a)	125.0(7)	O(21)−C(21)−O(22a)	124.1(9)

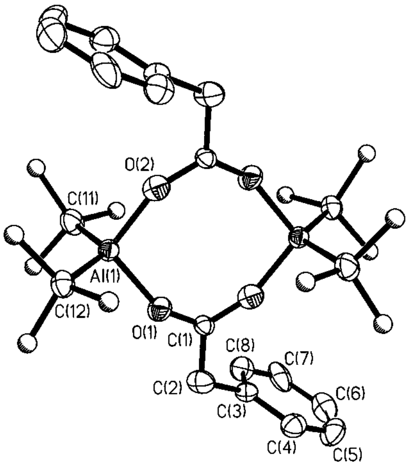

Figure 3. Molecular structure of $[(^tBu)_2Al(\mu\text{-}O_2CCH_2Ph)]_2$ (**4**). Thermal ellipsoids are shown at the 20% level. *tert*-Butyl methyl groups are shown as shaded spheres, and hydrogen atoms are omitted for clarity.

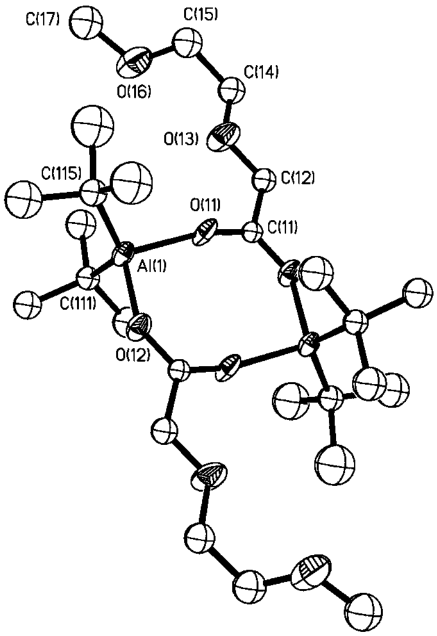

Figure 4. Molecular structure of one of the crystallographically independent molecules of $[(^tBu)_2Al(\mu\text{-}O_2CCH_2\text{-}OCH_2CH_2OCH_3)]_2$ (**9**). Thermal ellipsoids are shown at the 20% level, and hydrogen atoms are omitted for clarity.

This is as predicted previously for other alkylaluminum carboxylates from IR and Raman spectroscopy, mass spectrometry, and molecular weight measurements; see below.[13−16] The Al−O bond lengths to the carboxylate ligands in these dimeric systems [Al−O = 1.767(7)−1.837(6) Å] are within the range expected for four coordinate aluminum.[17] The carboxylate's O−C bond lengths in each compound are similar (see Tables 1−4), indicative of a symmetrically bound acid group that is unaffected by the carboxylate organic substituents. The bond lengths and angles within the carboxylate unit are typical of such moieties.[18] The ligand bite distances [Al(1)···Al(1a) = 4.217(2)−4.463(8) Å] are at the long end of the range previously observed for alkylaluminum carboxylates (3.26−4.18 Å).[11,19,20]

The carboxylate *tert*-butyl group in compound **1** shows a crystallographically imposed disorder, due to the presence of a mirror plane perpendicular to the $Al_2O_4C_2$

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(17) Haaland, A. *Coordination Chemistry of Aluminum*; Robinson G. H., Ed.; VCH: New York, 1993; Chapter 1.

(18) The carboxylate O−C−O unit in $[(^tBu)_2Al(\mu\text{-}O_2CCH_2Ph)]_2$ (**4**) shows a slight asymmetry: C(1)−O(1) < C(1)−O(2). This effect may be as a consequence of steric repulsion between the phenyl group and the aluminum *tert*-butyl groups.

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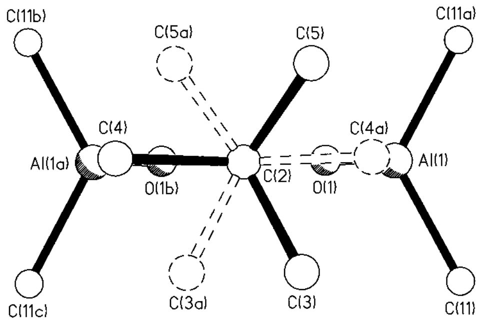


Figure 5. Partial coordination sphere of the of the $Al_2O_4C_2$ cycle in $[(^tBu)_2Al(\mu\text{-}O_2C^tBu)]_2$ (**1**) showing the crystallographic disorder. One of the structural isomers is indicated by open circles and dashed lines.

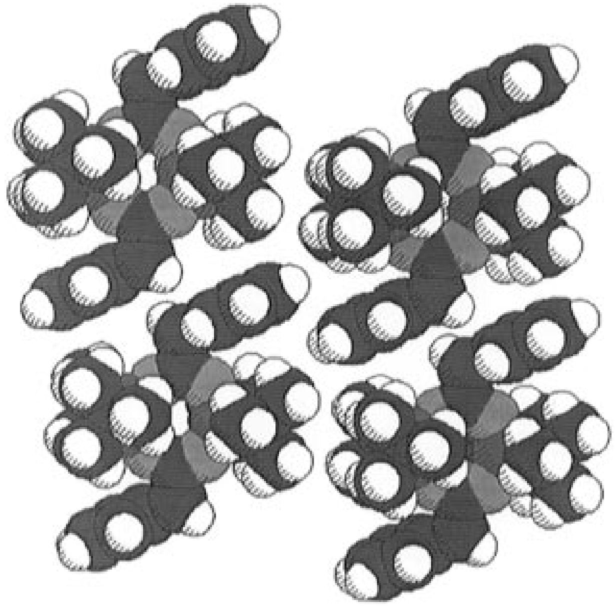
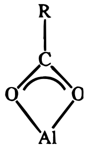


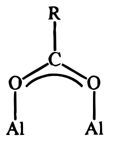
Figure 6. Molecular packing diagram of $[(^tBu)_2Al(\mu\text{-}O_2CCH_2Ph)]_2$ (**4**) viewed perpendicular to the $Al_2O_4C_2$ cycles.

plane; see Figure 5. The molecular packing of compounds **1**, **3**, and **9** show no unusual intermolecular interactions. In contrast, the packing arrangement of $[(^tBu)_2Al(\mu\text{-}O_2CCH_2Ph)]_2$ (**4**) exhibits a layered arrangement controlled by the presence of strong $\pi\cdots\pi$ stacking interactions; see Figure 6. The crystal structure may be considered to consist of double layers of the phenyl groups interspersed by an organometallic layer. The Ph···Ph intermolecular distances are 3.95 Å, similar to that observed for other group 13 aryl compounds.[21]

As discussed previously,[22,23] the ability to differentiate between chelating (**IV**) and bridging (**V**) bidentate modes of carboxylate coordination by IR spectroscopy is often difficult. However, the presence of bands in the IR spectra of compounds **1**−**10** at 1559−1489 cm^{-1} $[\nu_{asymm}(CO_2)]$ and 1496−1448 cm^{-1} $[\nu_{symm}(CO_2)]$[24] are consistent with the dimeric structures in the solid state. Importantly, they preclude unidentate coordination of a carboxylic acid group to aluminum whose IR spectrum would contain stretches at 1680−1640 and 1610−1570 cm^{-1}.[25,26] The presence of $M^+ - {}^tBu$ peaks, i.e., $[Al_2(^tBu)_3(O_2CR)_2]^+$, in the mass spectra of compounds **1**−**10** is also consistent with dimeric structures, i.e., **III**.

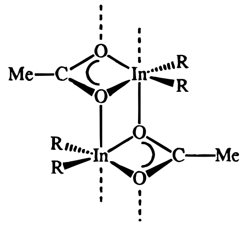


(IV)



(V)

Stability of Different Bonding Geometries of Carboxylate Ligands in Aluminum Compounds. Although aluminum carboxylate compounds, $Al(O_2CR)_3$, and carboxylate alumoxanes have been proposed to contain chelating carboxylate groups,[27,28] there has been no evidence for this mode of coordination to aluminum. To the best of our knowledge, all aluminum carboxylate complexes contain either terminal monodentate or bridging carboxylate ligands.[19,20,29,30] In fact, by analogy with the isolobal 1,3-diaryltriazenide compounds,[31] we have proposed that the chelate mode is unavailable for carboxylates on aluminum due to the ring strain which would be present in such a structure.[32] We note that the only examples of a chelating carboxylate for a group 13 metal to be crystallographically characterized are $[R_2In(\mu{:}\lambda^2\text{-}O_2CMe)]_\infty$ (R = Me,[33] Et[34]) in which the acetate ligand is both chelating and bridging (**VI**) and the O−C−O angles (119−120°) are similar to the "free" acid.



(VI)

In order to better understand the relative stability of monodentate, chelating and bridging carboxylate we

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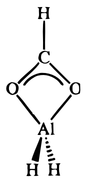
Table 5. Calculated Structural Parameters (Å, deg) for $[H_2Al(O_2CH)]_n$

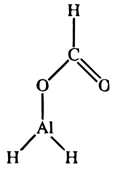
param	H_2Al (λ^2-O_2CH)	$H_2Al[OC(O)H]$		$[H_2Al$(μ-$O_2CH)]_2$[a]
		eclipsed	staggered	
Al−O	1.921	1.703	1.685	1.811
Al···O′		3.426	3.632	
Al−H	1.579	1.576, 1.576	1.577	1.582, 1.597
O−C	1.278	1.339	1.333	1.257
O′−C		1.199	1.198	
C−H	1.070	1.077	1.078	1.072
O−Al−O	67.84			109.8
O−Al−H	112.3	114.6, 120.9	117.8	104.1, 107.3
H−Al−H	125.5	124.4	124.4	123.8
Al−O−C	89.01	145.9	161.3	141.6
O−C−O	114.1	124.4	124.2	123.4
O−C−H	122.9	111.9	112.3	118.3
O′−C−H		123.6	123.5	

[a] Chair conformation.

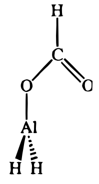
have performed *ab initio* calculations at the HF/3-21G(*) level (see Experimental Section) on the model compounds $H_2Al(\lambda^2\text{-}O_2CH)$ (**VII**), $H_2Al[OC(O)H]$ in



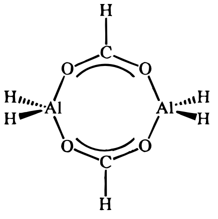
(VII)



(VIII)



(IX)



(X)

eclipsed (**VIII**) and *staggered* (**IX**) conformations, and $[H_2Al(\mu\text{-}O_2CH)]_2$ (**X**). The optimized calculated structural parameters for each model compound are given in Table 5, and the structures are shown in Figure 7a−d. The calculated O−C−O angle (114.1°) for the chelating carboxylate in $H_2Al(\lambda^2\text{-}O_2CH)$ is significantly smaller than observed for a free carboxylic acid[35] and consistent with our previous prediction.[32] In contrast, the O−C−O angles calculated for the terminal (124.2 and 124.4°) and bridging (123.4°) modes of coordination are unchanged from a free acid.

As was the case for $H_2Al(\lambda^2\text{-}O_2CH)$, there is no crystallographically characterized analog of the monodentate compounds, $H_2Al[OC(O)H]$, available for a direct comparison of the *ab initio* calculated structures. However, the calculated structures for both conformations are reasonable in comparison to the terminal carboxylate complex anion, $[Me_3Al\{OC(O)Me\}]^-$.[36] The Al−O bond distances in $H_2Al[OC(O)H]$ (1.685 and 1.703 Å) are shorter than those in $[Me_3Al\{OC(O)Me\}]^-$ [1.83(1) Å] consistent with a three-coordinate center in the former,[17] while the carboxylate ligand is within experimental error of the observed structures. However, it is interesting to note that while the aluminum is positioned *cis* to the carbonyl group in both conformations of $H_2Al[OC(O)H]$ (see Figure 7b,c), the aluminum is *cis* to the Me group in $[Me_3Al\{OC(O)Me\}]^-$ (see Figure 8a). This difference is clearly a function of the coordination number about aluminum, since the calculated structure for $[H_3Al\{OC(O)H\}]^-$ (**XI**), see Figure 8b, faithfully models all the observed structural features in $[Me_3Al\{OC(O)Me\}]^-$; see Table 6.

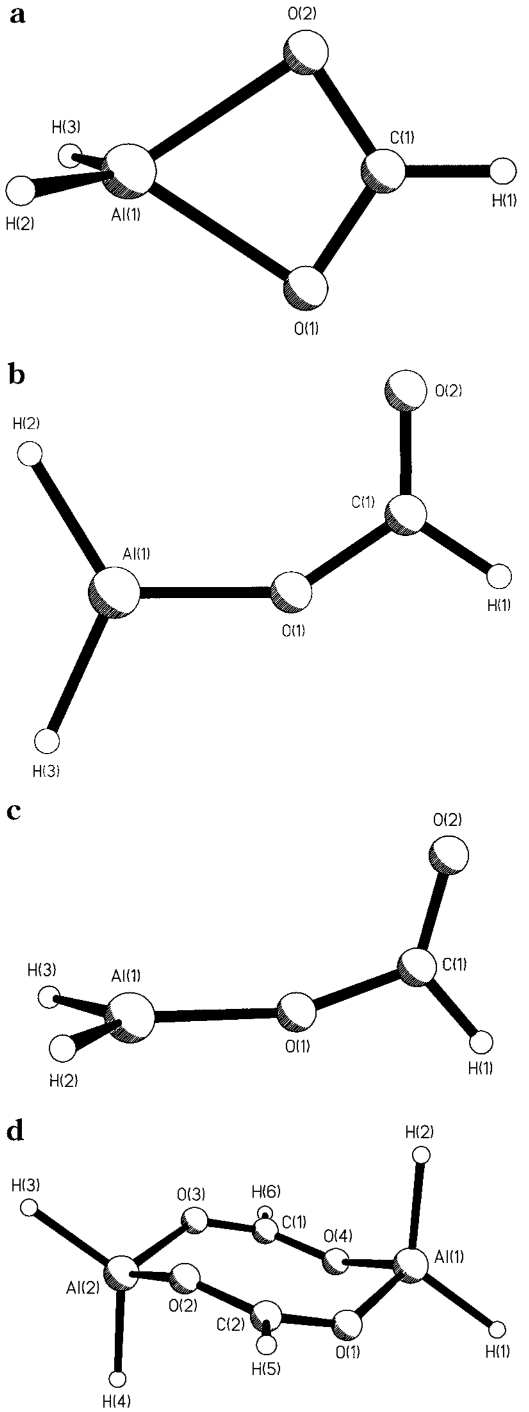
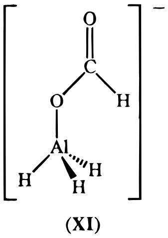


Figure 7. *Ab initio* HF/3-21G(*) calculated structures of (a) $H_2Al(\lambda^2\text{-}O_2CH)$, (b) *eclipsed*-$H_2Al[OC(O)H]$, (c) *staggered*-$H_2Al[OC(O)H]$, and (d) $[H_2Al(\mu\text{-}O_2CH)]_2$.



(XI)

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(35) See for example: (a) Schomaker, V.; O'Gorman, J. M. *J. Am. Chem. Soc.* **1947**, *69*, 2638. (b) Karle, J.; Brockway, L. O. *J. Am. Chem. Soc.* **1944**, *66*, 574. (c) Ladell, J.; McDonald, T. R. R.; Schmidt, G. M. J. *Acta Crystallogr.* **1964**, *17*, 1588. (d) Wierda, D. A.; Feng, T.; Barron, A. R. *Acta Crystallogr. C* **1989**, *45*, 338 and references therein.

(36) Atwood, J. L.; Hunter, W. E.; Crissinger, K. D. *J. Organomet. Chem.* **1977**, *127*, 403.

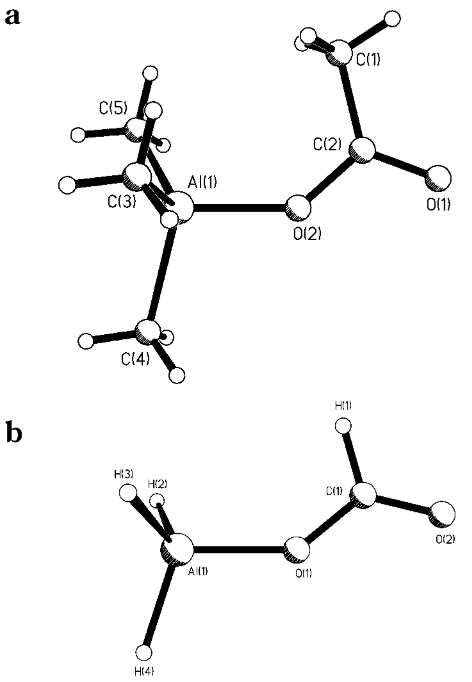

Figure 8. Comparison of the structure of (a) the $[Me_3Al(\lambda^1\text{-}O_2CMe)]^-$ anion and (b) the HF/3-21G(*) calculated structure of $[H_3Al\{OC(O)H\}]^-$.

Table 6. Structural Parameters for $[H_3Al\{OC(O)H\}]^-$ in Comparison to Experimental Values for $[Me_3Al\{OC(O)Me\}]^-$ [a]

param	$[H_3Al\{OC(O)H\}]^-$ calcd HF/3-21G(*)	$[Me_3Al\{OC(O)Me\}]^-$ XRD[b]
Al−O	1.791	1.83(1)
Al−H	1.639(av)	
C−O	1.301	1.32(2)
O′−C	1.214	1.23(2)
C−H	1.091	
H−Al−H	112.9(av)	112.4(av)[c]
H−Al−O	107.9(av)	106.4(av)[d]
Al−O−C	140.4	137(1)
O−C−O′	126.6	117(1)
O−C−H	113.8	118(1)[e]
O′−C−H	119.6	124(1)[e]

[a] Distances in Å, angles in deg. [b] X-ray diffraction; see: Atwood, J. L.; Hunter, W. E. *J. Organomet. Chem.* **1977**, *127*, 403. [c] C−Al−C. [d] C−Al−O. [e] O−C−C.

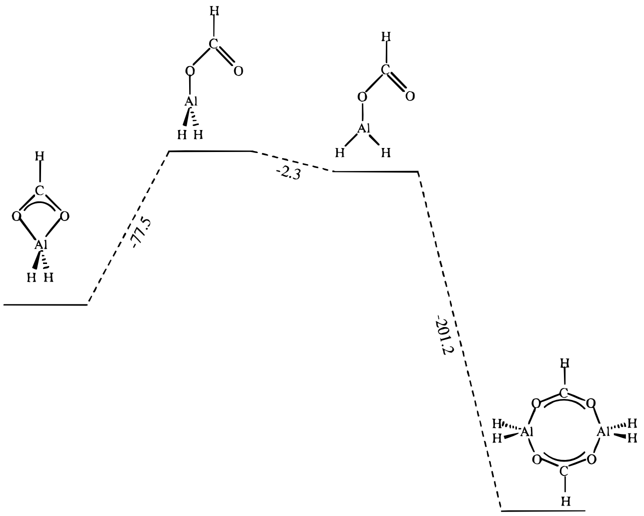

Figure 9. Calculated relative energy diagram for dialkylaluminum carboxylate compounds, $H_2Al(\lambda^2\text{-}O_2CH)$, *eclipsed*-$H_2Al[OC(O)H]$, *staggered*-$H_2Al[OC(O)H]$, and $[H_2Al(\mu\text{-}O_2CH)]_2$. Calculations are at the MP2/3-21G(*) level, and energies are given in kJ·mol^{-1}.

The total energies of the model compounds were determined at the MP2/3-21G(*) level for the optimized structures. As can be seen from Figure 9, the chelate carboxylate compound $H_2Al(\lambda^2\text{-}O_2CH)$ is in fact stabilized by −77.5 kJ·mol^{-1} with respect to the staggered monodentate conformation of $H_2Al[OC(O)H]$ (*cf.*, **IX**); however, this stabilization is insignificant as compared to the energy calculated ($\Delta H = -407$ kJ·mol^{-1}) for the model reaction eq 3.

$$2H_2Al[OC(O)H] \rightarrow [H_2Al(\mu\text{-}O_2CH)]_2 \qquad (3)$$

This value should be compared to the Al−O bond strength (512 kJ·mol^{-1}).[37] We note that although the chelate structure (**VII**) is unstable with respect to the dimeric structure (**X**) and the Lewis acid base complex (**XI**), it is stable with respect to the monomeric three-coordinate aluminum compounds (**VIII** and **IX**). Thus, a compound with a chelating carboxylate (*cf.*, **VII**) may be isolable in the absence of an external Lewis base, i.e., preclusion of the formation of a Lewis acid base adduct (**XI**), and if the substituents on aluminum are sufficiently large to preclude dimerization (**X**).

Ring Conformation and Carboxylate−Aluminum Bonding. The $Al_2O_4C_2$ cycles in $[(^tBu)_2Al(\mu\text{-}O_2CR)]_2$ are examples of eight-membered ring compounds of the group 13 metals.[38] The eight-membered $Al_2O_4C_2$ ring is flat in compound **1** but adopts a chairlike conformation in compounds **3**, **4**, and **9**.[39] The difference between flat and the most puckered ring is clearly seen in a comparison of Figures 5 and 10. The puckering of the $Al_2O_4C_2$ ring may be considered to be as a result of folding of the eight-membered ring along the two interligand O···O vectors. The extent of folding (θ_{ring}) is defined as the angle between the AlO_2 planes and the O_4C_2 plane. For aluminum carboxylates, $[(^tBu)_2Al(\mu\text{-}O_2CR)]_2$, the geometrical result of the planar $Al_2O_4C_2$ core is that the Al···Al intramolecular distance is maximized and, consequently, so are the intersubstituent distances, i.e., ^{t}Bu···R. Therefore, when the alkyl group on aluminum is the bulky *tert*-butyl group, the presence of sterically hindered groups at the carboxylate (R) should promote a flat conformation. This is indeed observed with a correlation between θ_{ring} and the steric bulk of the carboxylate substituent (R) as defined by Tolman's cone angle, θ; see Figure 11.[40] The values calculated for $[H_2Al(\mu\text{-}O_2CH)]_2$ at the STO-3G and 3-21G(*) levels are included in Figure 11 for comparison.

The observation that there exists a correlation between the extent of the puckering of the $Al_2O_4C_2$ ring

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[37] Dean, J. A. *Lange's Handbook of Chemistry*, 14th ed.; McGraw-Hill: New York, 1992.

[38] See: (a) Haiduc, I. *The Chemistry of Inorganic Ring Systems*; Wiley: Chichester, U.K., 1970; Vol. II, Chapter 7, p 1018. (b) Cesari, M.; Cucinella S. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerly, D. B., Eds.; Academic Press: New York, 1987; Vol. 2, p 167. (c) Oliver, J. P.; Kumar, R.; Taghiof, M. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; Chapter 5, p 167. (d) Hausen, H. D.; Gerstner, F.; Schwarz, W. *J. Organomet. Chem.* **1978**, *145*, 277.

[39] Similar chairlike conformations have been observed for the gallium diphenylphosphinate compounds $[R_2Ga(\mu\text{-}O_2PPh_2)]_2$; see: (a) Hahn F. E.; Schneider, B. *Z. Naturforsch. B* **1990**, *45*, 134. (b) Landry, C. C.; Hynes, A.; Barron, A. R.; Haiduc, I.; Silvestru, C. *Polyhedron* **1996**, *15*, 391.

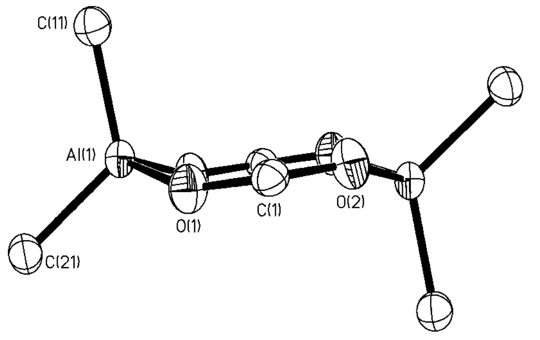


Figure 10. Eight-membered cyclic core of $[(^t\text{Bu})_2\text{Al}(\mu\text{-O}_2\text{CPh})]_2$ (**3**) demonstrating the chairlike conformation of the $\text{Al}_2\text{O}_4\text{C}_2$ cycle.

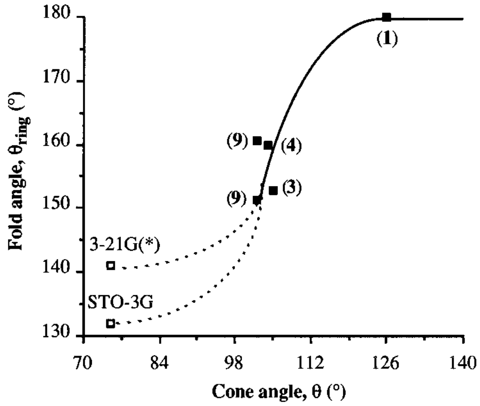
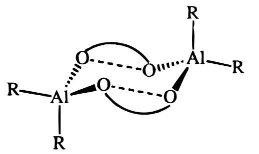
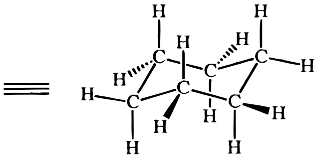


Figure 11. Plot of the folding of the $\text{Al}_2\text{O}_4\text{C}_2$ cycle (θ_{ring}, deg) in dialkylaluminum carboxylates, $[(^t\text{Bu})_2\text{Al}(\mu\text{-O}_2\text{CR})]_2$, versus Tolman's cone angle, θ, of the carboxylate substituent (deg). The values calculated at the HF/3-21G(*) and HF STO-3G levels for $[\text{H}_2\text{Al}(\mu\text{-O}_2\text{CH})]_2$ are included for comparison. The numbering of points corresponds to the compounds described in the text.

with the steric bulk of the carboxylate alkyl substituent, R, raises the following question: Why is a puckered conformation stable? In particular, a simplistic VSEPR picture of the bonding in $[(^t\text{Bu})_2\text{Al}(\mu\text{-O}_2\text{CR})]_2$ suggests that a flat structure allows for bonding between a sp^2 lone pair orbital on the carboxylate and an empty sp^3 orbital on aluminum. Given that the carboxylate $\text{O}\overset{...}{-}\text{C}\overset{...}{-}\text{C}$ unit is rigid and planar as a consequence of the sp^2 central carbon, the $\text{Al}_2\text{O}_4\text{C}_2$ ring in $[(^t\text{Bu})_2\text{Al}(\mu\text{-O}_2\text{CR})]_2$ may in fact be defined by a Al_2O_4 cycle (**XII**), whose structure is clearly analogous to cyclohexane (**XIII**).



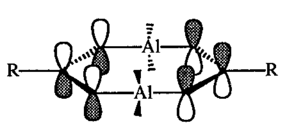
(XII)



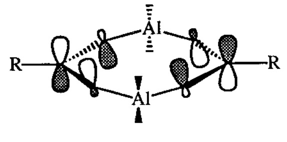
(XIII)

Cyclohexane is perhaps the most important of the carbocycles due to its ability to adopt an essentially strain-free chair conformation. In this structure the bond angles are all close to tetrahedral and all C−H and C−C bonds are staggered with respect to each other, thus minimizing both bond angle strain and bond pair−bond pair electron repulsions. It would appear therefore that the puckered chairlike conformation preferred by $[(^t\text{Bu})_2\text{Al}(\mu\text{-O}_2\text{CR})]_2$ (in the absence of steric hindrance) is a consequence of the desire to minimize ring strain and position the Al−C and Al−O bonds staggered with respect to the C−O bond, oxygen lone pair, and C=O π-bonding electrons.[41]

The electronic consequence of the chairlike conformation is to change the hybridization at the carboxylate oxygen from sp^2 toward sp^3 and, consequently, destabilize the C−O π-bond. Comparison of the average C−O bond distances in compounds **1**, **3**, **4**, and **9** shows that with increased folding of the chair (i.e., from 180 to 152.9°) there is an increase in the average C−O bond lengths (e.g., from 1.235 to 1.256 Å) consistent with this view. *Ab initio* calculations at the MP2/3-21G(*) level on the planar and puckered conformations suggest that, upon increased folding of the chair, the carboxylate π-orbital changes from being C(p)−O(p)−O(p) in character (i.e., **XIV**) to C(sp^x)−O(p)−C(sp^x), **XV**.



(XIV)



(XV)

Di-*tert*-butylaluminum Carboxylates as Model Compounds for Carboxylate Alumoxanes. As discussed in the Introduction, previously published work from our laboratory demonstrated the similarity of the pentaaluminum cage compound $[\text{Al}_5(^t\text{Bu})_5(\mu_3\text{-O})_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CPh})_2]$ to the surface of carboxylate alumoxanes.[11] If the carboxylate alumoxanes, $[\text{Al(O)}_x(\text{OH})_y(\text{O}_2\text{CR})_z]_n$, could be represented by a suitable and simpler model, i.e., $[(^t\text{Bu})_2\text{Al}(\mu\text{-O}_2\text{CR})]_2$, subsequent structure−property relationships and reactivity studies could be simplified. Since the carboxylate alumoxanes consist of a boehmite-like core on whose surface the carboxylate ligands are bound,[2,3] any model compound must suitably mimic the structural features of the surface of the boehmite core, predominantly the Al···Al distance.

Table 7 represents a comparison of the spectroscopic and structural data available for carboxylate compounds of aluminum, facilitating a direct comparison of the various potential model compounds with carboxylate alumoxanes. The IR spectra clearly shows that $[(\text{R}')_2\text{Al}(\mu\text{-O}_2\text{CR})]_2$ (R′ = Me, Et, ^{t}Bu),[13−16] $[\text{Al}_5(^t\text{Bu})_5(\mu_3\text{-O})_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CPh})_2]$,[11] $[\text{Al}_6(^t\text{Bu})_6(\mu_3\text{-O})_4(\mu\text{-OH})_2(\mu\text{-O}_2\text{CCCl}_3)_2]$ (**XVI**),[19] and the carboxylate alumoxanes, $[\text{Al(O)}_x(\text{OH})_y(\text{O}_2\text{CR})_z]_n$,[2,3] all contain bridging carboxylates. Unfortunately, IR spectroscopy and ^{13}C NMR spectra cannot be used to differentiate monodentate versus bridging carboxylate ligation on aluminum because there appears no correlation between the spectroscopic values and the Al···Al ligand bridging distance. It is also important to note that the O−C−O angle appears to be unaffected by the ligand bite distance, suggesting that with near-

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[40] The Tolman cone angle for CH_2Ph (104°) is smaller than that measured from the X-ray crystal structure of $[(^t\text{Bu})_2\text{Al}(\mu\text{-O}_2\text{CCH}_2\text{Ph})]_2$ (110°); see: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[41] It should be noted that while the activation enegy of the chair-to-chair conformational exchange in cyclohexane (10.79 kJ·mol^{-1}) may be obtained from NMR measurements (see: Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York, 1969), the exchange in $[(^t\text{Bu})_2\text{Al}(\mu\text{-O}_2\text{CR})]_2$ is not frozen out at −95 °C.

Table 7. Spectroscopic and Structural Data for Aluminum Carboxylate Compounds

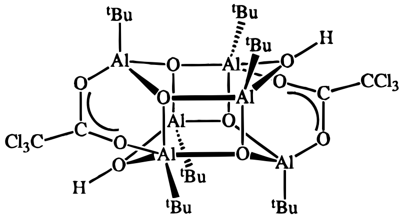
compd	IR (cm^{-1}) asymm	IR (cm^{-1}) symm	^{13}C NMR O_2CR (ppm)	Al···Al (Å)	O–C–O (deg)	source
$[(^tBu)_2Al(\mu\text{-}O_2CR)]_2$	1559–1489	1496–1448	173–189	4.217(2)–4.463(8)	122.1(4)–125.0(7)	*e*
$[Et_2Al(\mu\text{-}O_2CR)]_2$	1628–1545	1474–1425	173–185	*d*	*d*	*f*
$[Me_2Al(\mu\text{-}O_2CR)]_2$	1550–1546	1480–1483	173–179	*d*	*d*	*g*
$Al(O_2CR)(salen)^a$	1680–1640	1610–1570	171–177	n/a	*d*	*g,h*
$[Al_5(^tBu)_5(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CPh)_2]$	1569	1496	173.1	3.242(1)	123.7(5)	*i*
$[Al_6(^tBu)_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2(\mu\text{-}O_2CCCl_3)_2]$	*b*	1467	*c*	3.11(3)	126.4(4)	*j*
$[Al_2(\mu\text{-}OH)(\mu\text{-}O_2CPh)_2\{MeC(O)OEt\}]^{3+}$	1690	1630	*c*	3.311(5)	*c*	*k*
$[Al(O)_x(OH)_y(O_2CR)_z]_n$	1596–1568	1496–1466	172–184	*d*	*d*	*h*

[a] H_2salen = *N,N′*-ethylenebis(salicylideneamine). [b] Not observed. [c] Data not reported. [d] Data not available. [e] This work. [f] Pietrzykowski, A.; Pasynkiewicz, S.; Poplawska, J. *Main Group Met. Chem.* **1996**, *18*, 651. [g] Landry, C. C.; Davis, J. A.; Apblett, A. W.; Barron, A. R. *J. Mater. Chem.* **1993**, *3*, 597. [h] Gurian, P. L.; Cheatham, L. K.; Ziller, J. W.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1991**, 1449. [i] Koide, Y.; Barron, A. R. *Organometallics* **1995**, *14*, 4026. [j] Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 2213. [k] Sobota, P.; Mustafa, M. O.; Utko, J.; Lis, T. *J. Chem. Soc., Dalton Trans.* **1990**, 1809.

Table 8. Comparison of Calculated Structural Parameters for Carboxylate Groups Bound to Boehmite and Isolated Carboxylate Compounds of Aluminum

compd	Al···Al (Å)	Al–O–C (deg)	source
boehmite (100)	2.86	≈128	*a*
	3.70	≈143	*a*
	4.68	≈161	*a*
boehmite (211)	3.11	≈133	*a*
$[(^tBu)_2Al(\mu\text{-}O_2CR)]_2$	4.21–4.46	134–172	*b*
$[Al_5(^tBu)_5(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CPh)_2]$	3.24	134 (av)	*c*
$[Al_6(^tBu)_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2(\mu\text{-}O_2CCCl_3)_2]$	3.11	128 (av)	*d*
$[Al_2(\mu\text{-}OH)(\mu\text{-}O_2CPh)_2\{MeC(O)OEt\}]^{3+}$	3.33	135 (av)	*e*

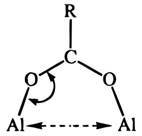
[a] Calculated from the structure of boehmite; see: Milligan, W. D.; McAtee, J. L. *J. Phys. Chem.* **1956**, *60*, 273. [b] This work. [c] Koide, Y.; Barron, A. R. *Organometallics* **1995**, *14*, 4026. [d] Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 2213. [e] Sobota, P.; Mustafa, M. O.; Utko, J.; Lis, T. *J. Chem. Soc., Dalton Trans.* **1990**, 1809.



(XVI)

invariant O–C and Al–O bond distances, the Al–O–C angle is the only covariable with Al···Al distance.

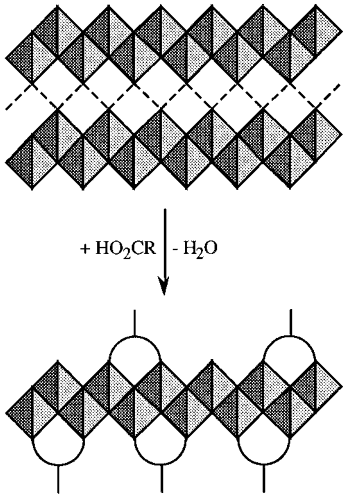
Table 8 lists the Al···Al distances found in boehmite[42] and aluminum carboxylate compounds along with the measured and predicted Al–O–C bond angles.[43] Thus, the suitability of a model complex must be based upon the ligand bridging distance (Al···Al), in comparison to the Al···Al distances present in boehmite, and the subsequent Al–O–C angle (*cf.*, **XVII**).



(XVII)

We have previously proposed that the carboxylate alumoxanes, prepared from the reaction of boehmite with carboxylic acids, are formed as a consequence of the cleavage of the interlayer hydrogen bonds in the (100) plane of boehmite; see Scheme 1. We propose that the reaction of carboxylic acids with the double-layered aluminum oxide hydroxide (boehmite) may be ideally considered as an intercalation/exchange reaction where the acid replaces some of the hydroxyl groups on the oxide double layer surface and bridges other aluminum sites. The substitution reaction leads to what results in an exfoliation/delamination reaction (Scheme 1) of the boehmite layers. This is similar to delaminated MoS_2 from the hydrolysis of M_xMoS_2.[44] The carboxylate alumoxanes are therefore nano-sized[2] exfoliated surface modified fragments of boehmite.

Scheme 1. Pictorial Representation of the Reaction of Boehmite with Carboxylic Acids[a]



[a] The shaded triangles represent a side view of the aluminum–oxygen fused octahedra, while the carboxylate groups are represented by a semicircle and bar.

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(42) Milligan, W. D.; McAtee, J. L. *J. Phys. Chem.* **1956**, *60*, 273.

(43) The estimated Al–O–C angles for carboxylate groups bound to boehmite are calculated on the basis of a planar Al_2O_2C unit, with Al–O and O–C distances of 1.85 and 1.25 Å, respectively, and a O–C–O angle of 123°.

(44) See for example: (a) Murphy, D. W.; DiSalvo, F. J.; Hull, G. W.; Waszczak, J. V. *Inorg. Chem.* **1976**, *15*, 17. (b) Bissessur, R.; Heising, J.; Hirpo, W.; Kanatzidis, M. *Chem. Mater.* **1996**, *6*, 318 and references therein.

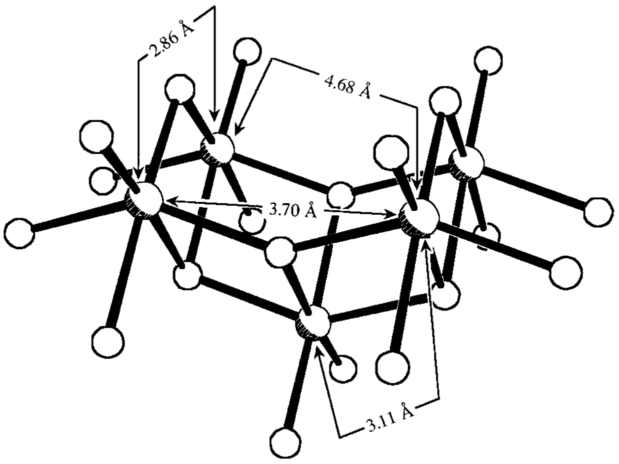

Figure 12. Pictorial representation of the structure of boehmite, showing the possible sites for carboxylate binding in the (100) and (211) planes. Aluminum and oxygen atoms are shown as shaded and open spheres, respectively.

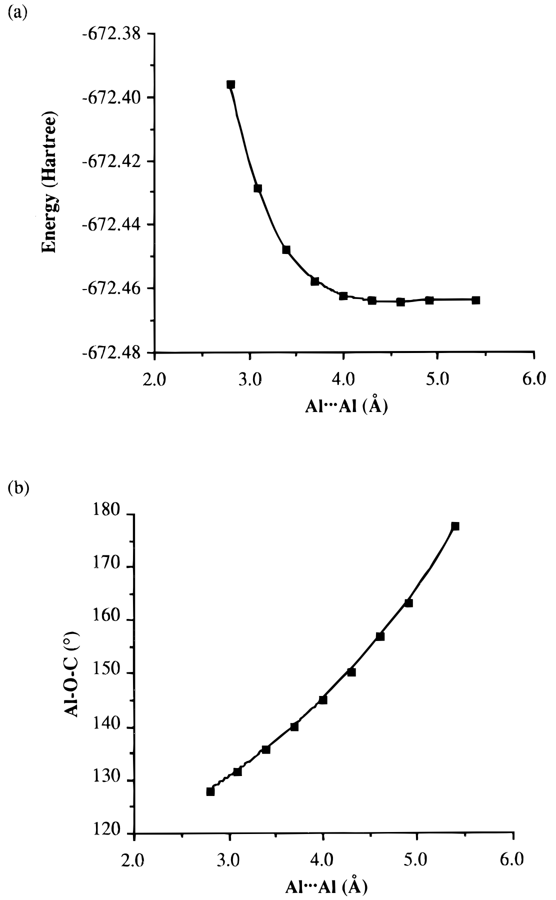

Figure 13. Plots of (a) the total energy calculated at the MP2/3-21G(*) level (hartrees) and (b) the subsequently optimized Al−O−C bond angle (deg), as a function of Al···Al distance (Å) for the model anion $[(H_3Al)_2(\mu\text{-}O_2CH)]^-$ (**XVIII**).

A consideration of the possible Al···Al distances on the (100) face of boehmite (see Figure 12) shows that three different inter-aluminum distances are possible, 2.86, 3.70, and 4.68 Å. The smallest Al···Al distance on the (100) plane of boehmite is optimum for a bridging hydroxide,[45] while the longest (4.68 Å) is larger than previously observed for bridging aluminum carboxylates. Thus, as we have previously proposed, the carboxylate moieties in carboxylate alumoxanes bridge the adjacent edge-shared octahedra (Al···Al = 3.70 Å). This value is close to the median of the Al···Al distances observed for $[({}^tBu)_2Al(\mu\text{-}O_2CR)]_2$ [4.217(2)−4.463(8) Å] and $[Al_5({}^tBu)_5(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CPh)_2]$ (3.24 Å). Thus, while not exact as a model for the surface carboxylate groups in alumoxanes, we propose that the dimeric dialkylaluminum carboxylates, $[({}^tBu)_2Al(\mu\text{-}O_2CR)]_2$ (**III**), represent a good working model systems.

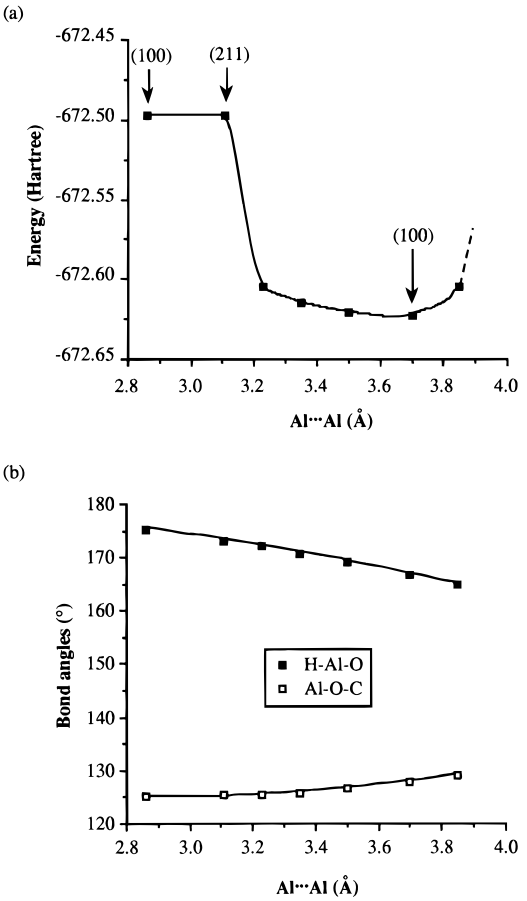

Figure 14. Plots of (a) the total energy calculated at the MP2/3-21G(*) level (hartrees) and (b) the subsequently optimized H_{trans}−Al−O and Al−O−C bond angles (deg), as a function of Al···Al distance (Å) for the model anion $[(H_5\text{-}Al)_2(\mu\text{-}O_2CH)]^{5-}$ (**XIX**). The Al···Al distances present on the (100) and (211) crystallographic planes of boehmite are marked.

We note that the ends of the core of the carboxylate alumoxanes will be derived from the (211) plane of boehmite, for which a short Al···Al distance is observed (3.11 Å); see Figure 12. This is within experimental error of the value observed for $[Al_6({}^tBu)_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2(\mu\text{-}O_2CCCl_3)_2]$,[19] suggesting that compounds of the general formula $[Al_6({}^tBu)_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2(\mu\text{-}O_2CR)_2]$ (**XVI**) are better models of the edges/ends of the carboxylate alumoxane than $[({}^tBu)_2Al(\mu\text{-}O_2CR)]_2$. The carboxylate alumoxanes $[Al_6({}^tBu)_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2(\mu\text{-}O_2CR)_2]$ may be readily prepared from the cage opening of $[({}^tBu)Al(\mu_3\text{-}O)]_6$ (eq 4).[11]

$$[({}^tBu)Al(\mu_3\text{-}O)]_6 + 2RCO_2H \rightarrow [Al_6({}^tBu)_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2(\mu\text{-}O_2CR)_2] \quad (4)$$

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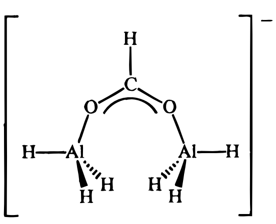
[45] Harlan, C. J.; Mason, M. R.; Barron, A. R. *Organometallics* **1994**, *13*, 2957.

Molecular Modeling Studies on the Fitness of Carboxylic Acids for the Formation of Alumoxanes from Boehmite. The formation of carboxylate alumoxanes from the reaction of the mineral boehmite with a carboxylic acid is unique. Attempts to prepare other alumoxane derivatives via similar routes have been unsuccessful. For example, reaction of boehmite with β-diketones yields the monomeric β-diketonate complexes, i.e., $Al(acac)_3$. This observation begs the following question: *Why are carboxylic acids ideally suited for the formation of alumoxanes from boehmite?*

From the data shown in Tables 7 and 8 it would appear that one advantage of the carboxylate anion is its ability to act as a bridging ligand over a wide range of Al···Al distances. This is confirmed by *ab initio* calculations for the model anion $[(H_3Al)_2(\mu\text{-}O_2CH)]^-$ (**XVIII**). Figure 13 shows the total energy, calculated by *ab initio* methods MP2/3-21G(*) (Figure 13a), and the subsequently optimized Al−O−C bond angle (Figure 13b), as a function of Al···Al distance for $[(H_3Al)_2(\mu\text{-}O_2CH)]^-$.[46] On the basis of these results, we propose that the carboxylate ligand can readily act as a bridging ligand in binuclear aluminum compounds with a ligand bite distance within an Al···Al distance from 3.4 to 5.4 Å, without significant sacrifice of energy. The upper value will, however, be modified by the bonding requirements of 6-coordinate aluminum centers on the surface of a boehmite-like core of a carboxylate alumoxane.


(XVIII)

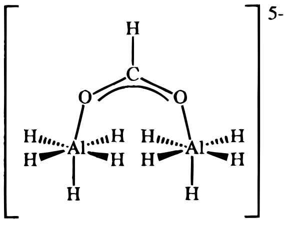

(XIX)

Figure 14 shows (a) the total energy calculated by *ab initio* methods MP2/3-21G(*), and (b) the optimized structural parameters, as a function of Al···Al distance for the model anion $[(H_5Al)_2(\mu\text{-}O_2CH)]^{5-}$ (**XIX**). The Al···Al distances found in boehmite are shown for comparison in Figure 14a. The bonding requirements of two adjacent 6-coordinate aluminums limit the stable range of a bridging carboxylate to an Al···Al distance of between 3.2 and 3.8 Å.

On the basis of the data shown in Figure 14b, it may be estimated that for a carboxylate to bridge across the longest Al···Al distance on the (100) plane of boehmite (4.6 Å) the *trans*-O_{oxide}−Al−$O_{carboxylate}$ and Al−O−C angles would be required to be *ca.* 153 and 138°, respectively. Such a geometry would clearly result in significant bond strain at aluminum, as is confirmed by the instability of the model compound (Figure 14a). However, a carboxylate ligand is nearly ideal to act as a bridging ligand across the 3.7 Å Al···Al distance of the (100) face of boehmite. It is interesting to speculate, with hindsight, that this observation provides a rationalization for the suitability of carboxylic acids for the selective formation of self-assembled monolayers on alumina.[47] We propose that the reaction of a carboxylic acid (or carboxylate) with the surface of boehmite and alumina be considered a topotactic reaction, since no reconstruction (bulk reorganization) of the Al−O framework is required for the carboxylate group to bind.

Conclusion

We have reported the first structural characterization of dialkylaluminum carboxylates, $[(^tBu)_2Al(\mu\text{-}O_2CR)]_2$, which confirms their dimeric, carboxylate-bridged structures. The formation of a carboxylate-bridged dimer, rather than a monomer with a chelating carboxylate ligand, may be rationalized in terms of the strain associated with the AlO_2C cycle. However, if dimerization could be precluded, then chelating coordination of the carboxylate is energetically preferred over a three-coordinate aluminum compound. The eight-membered $Al_2O_4C_2$ cycle in $[(^tBu)_2Al(\mu\text{-}O_2CR)]_2$ adopts a chairlike conformation (reminiscent of cyclo-hexane) in order to minimize angle strain and bond pair−bond pair electron repulsions. The extent of ring folding in the solid state is related to the steric bulk of the substituents on the carboxylate group (R); the smaller the substituent, the greater the folding of the chair.

The Al···Al bridging distances observed for $[(^tBu)_2Al(\mu\text{-}O_2CR)]_2$ [4.217(2)−4.463(8) Å] are somewhat larger than the value expected for a carboxylate bound to the (100) surface of boehmite (3.70 Å) as would be observed in the carboxylate alumoxanes. Despite this, the dialkylaluminum carboxylate compounds, $[(^tBu)_2Al(\mu\text{-}O_2CR)]_2$, are suitable models for the spectroscopic characterization of carboxylate alumoxanes. In addition, they appear to be a good initial model to probe reaction chemistry of carboxylate alumoxanes.

The ubiquitous nature of carboxylic acids, and their derived carboxylate anions, in the chemistry of aluminum may be related to their ability to bind to the surface of aluminum oxides without requiring any bulk reconstruction. Thus, we may conclude the carboxylate ligand is ideally suited for surface binding and reaction with aluminum oxides.

Experimental Section

Unless otherwise stated, all manipulations were carried out under either prepurified nitrogen or argon. All solvents were distilled from sodium−benzophenone ketyl solution and degassed immediately before use. $Al(^tBu)_3$ was prepared as previously described.[48] All acids (except for $HO_2CCH_2OCH_3$, $HO_2CCH_2OCH_2CH_2OCH_3$, and $HO_2CCH_2(OCH_2CH_2)_2OCH_3$, which were used without purification) were purified by distillation or crystallization. Melting points were obtained on a Seiko 200 TG/DTA instrument using a carrier gas of dry nitrogen. The ramp rate was 5 °C·min^{-1} for all samples, with a data collection of 1 s^{-1}. Mass spectra were obtained by using a Finnigan MAT 95 mass spectrometer and associated data system. IR spectra (4000−400 cm^{-1}) were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer as Nujol mulls. ^1H and ^{13}C NMR spectra were obtained on Bruker AM-250 spectrometer, and chemical shifts are reported in ppm relative to external $SiMe_4$. Elemental analysis were performed using

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[46] We note that the *anti*−*anti* geometry observed in the crystal structure of the anion, $[(Me_3Al)_2(\mu\text{-}O_2CMe)]^-$,[30] is in fact preferred by *ca.* 30 kJ·mol^{-1}; however, since we are interested in the ability of a carboxyalte group to bridge two aluminum atoms on a surface, only *syn*−*syn* geometries are included in the data presented in Figure 13.

[47] For example, see: Laibinis, P. D.; Hickman, J. J.; Wrighton, M. S.; Whitesides, G. M. *Science* **1989**, *245*, 845.

[48] (a) Uhl, W. *Z. Anorg. Allg. Chem.* **1989**, *570*, 37. (b) Lehmkuhl, H.; Olbrysch, O.; Nehl, H. *Liebigs Ann. Chem.* **1973**, 708. (c) Lehmkuhl, H.; Olbrysch, O. *Liebigs Ann. Chem.* **1973**, 715.

a Perkin-Elmer Magna 400 ICP atomic emission spectrometer. All compounds were digested in nitric acid. *Caution: Digestion of organoaluminum compounds in acidic solutions should be undertaken with care.*

[(^{t}Bu)$_2$Al(μ-O$_2$C^{t}Bu)]$_2$ (1). HO$_2$C^{t}Bu (1.26 g, 12.3 mmol) was suspended in hexane (50 mL) and cooled to −78 °C. Upon dropwise addition of Al(^{t}Bu)$_3$ (2.44 g, 3.10 mL, 12.3 mmol), the solution became clear and gas evolution was observed. The reaction mixture was allowed to warm to room temperature with stirring. After standing overnight, the reaction mixture was reduced under vacuum, and the solution was cooled to −29 °C, from which large crystals grew overnight. Yield: 2.49 g, 10.3 mmol, 84%. Mp: 103 °C. Anal. Found (calc): Al, 11.0 ± 0.2 (11.1). MS (EI, %): *m/z* 469 ($M^+ -$ Me, 4), 27 ($M^+ -$ ^{t}Bu, 100), 370 ($M^+ -$ 2^{t}Bu, 6). IR (cm^{-1}): 2925 (s), 2832 (s), 2760 (m), 2728 (m), 2698 (m), 2626 (w), 2367 (w), 2166 (w), 2051(w), 1984 (w), 1830 (m), 1739 (m), 1603 (s), 1490 (s), 1448 (s), 1383 (s), 1362 (s), 1233 (s), 1197 (m), 1174 (w), 1069 (m), 1034 (w). ^{1}H NMR: δ 1.14 [18H, s, Al−C(CH_3)$_3$], 1.07 [9H, s, O$_2$CC(CH_3)$_3$]. ^{13}C NMR: δ 189.0 (O$_2$$C$), 30.0 [Al−C($CH_3$)], 27.4 [O$_2$CC($CH_3$)].

[(^{t}Bu)$_2$Al(μ-O$_2$CCCl$_3$)]$_2$ (2). This was prepared in a similar manner to compound **1**, except a pale yellow solid was isolated and recrystallized from CH$_2$Cl$_2$ (30 mL). Yield: 80%. Mp: 109 °C. Anal. Found (calc): Al, 8.5 ± 0.2 (8.8). MS (EI, %): *m/z* 547 ($M^+ -$ ^{t}Bu, 15), 493 ($M^+ -$ 2^{t}Bu, 100). IR (cm^{-1}): 3312 (w), 3129 (w), 3062 (w), 2946 (s), 2924 (s), 2907 (s) 2866 (m), 2837 (s), 2765 (w), 2734 (w), 2704 (w), 2628 (w), 2360 (w), 2344 (w), 2172 (w), 1692 (s), 1559 (w), 1516 (w), 1461 (s), 1431 (s), 1386 (w), 1363 (w), 1263 (w), 1234 (w), 1197 (w), 1176 (w), 1157 (w), 1096 (w), 1004 (m), 908 (s), 991 (w), 939 (w), 863 (s), 834 (m), 818 (m), 812 (m), 736 (m), 686 (s), 616 (m), 581 (m), 531 (w), 491(m). ^{1}H NMR: δ 1.00 [18H, s, Al−C(CH_3)$_3$]. ^{13}C NMR: δ 29.1 [Al−C(CH$_3$)$_3$], 15.0 (CCl$_3$).

[(^{t}Bu)$_2$Al(μ-O$_2$CPh)]$_2$ (3). This was prepared in a similar manner to compound **1**. Yield: 80%. Mp: 257 °C. Anal. Found (calc): Al, 11 ± 1 (10.3). MS (EI, %): *m/z* 467 ($M^+ -$ ^{t}Bu, 5). IR (cm^{-1}): 2934 (w), 2917 (m), 2905 (m), 2829 (s), 1624 (m), 1614 (m), 1572 (m), 1493 (m), 1449 (s), 1429 (s), 1180 (w), 1025 (w), 1001 (w), 814 (m), 716 (m), 679 (w), 607 (w). ^{1}H NMR: δ 8.19 [2H, d, J(H−H) = 8.0 Hz, *o*-CH, Ph], 7.73 [1H, t, J(H−H) = 8.0 Hz, *p*-CH, Ph], 7.56 [2H, t, J(H−H) = 8.0 Hz, *m*-CH, Ph], 0.97 [18H, s, C(CH_3)$_3$]. ^{13}C NMR: δ 172.9 (O$_2$$C$), 135.3, 131.2, 129.0 ($C_6H_5$), 29.7 [C($CH_3$)$_3$], 15.0 [$C$(CH$_3$)$_3$].

[(^{t}Bu)$_2$Al(μ-O$_2$CCH$_2$Ph)]$_2$ (4). This was prepared in a similar manner to compound **1**. Yield: 82%. Mp: 110 °C. Anal. Found (calc): Al, 9.7 ± 0.3 (9.8). MS (EI): *m/z* 495 ($M^+ -$ ^{t}Bu, 100). IR (cm^{-1}): 3090 (m), 3062 (m), 3028 (m), 2922 (s), 2828 (s), 2757 (w), 2698 (w), 2729 (w), 1670 (w), 1947 (w), 1876 (w), 1804 (w), 1629 (s), 1588 (s), 1494 (s), 1459 (s), 1400 (s), 1304 (m), 1262 (s), 1195 (m), 1095 (s), 1027 (s), 936 (w), 912 (w), 847 (m), 808 (s), 758 (m). ^{1}H NMR: δ 7.02 (5H, m, C$_6$$H_5$), 3.30 (2H, s, C$H_2$), 1.04 [18H, s, C(C$H_3$)$_3$]. ^{13}C NMR: δ 180.9 (O$_2$$C$), 129.8 (*o*-$CH, C_6H_5$), 129.6 (*m*-$CH, C_6H_5$), 127.8 (*p*-$CH, C_6H_5$), 44 ($CH_2$), 29.8 [C($CH_3$)$_3$].

[(^{t}Bu)$_2$Al(μ-O$_2$CCHPh$_2$)]$_2$ (5). This was prepared in a similar manner to compound **1**. Yield: 78%. Mp: 104 °C. Anal. Found (calc): Al, 7.8 ± 0.3 (7.7). MS (EI): *m/z* 704 (M^+, 4), 647 ($M^+ -$ ^{t}Bu, 100). IR (cm^{-1}): 3388 (m), 3086 (m), 3062 (m), 2964 (s), 2935 (m), 2873 (m), 2835 (w), 2362 (w), 2343 (w), 1942 (w), 1733 (w), 1699 (m), 1683 (m), 1653 (s), 1636 (s), 1616 (s), 1589 (s), 1577 (s), 1570 (s), 1559 (s), 1506 (m), 1497 (s), 1457 (s), 1436 (s), 1386 (m), 1362 (m), 1339 (w), 1259 (s), 1191 (w), 1157 (w), 1081 (s), 1031 (s), 844 (m), 800 (s), 742 (s), 721 (s), 698 (s), 653 (s), 586 (m), 478 (m). ^{1}H NMR: δ 7.2 [4H, d, J(H−H) = 8.0 Hz, *o*-CH, Ph], 7.0 [4H, dd, J(H−H) = 8.0 Hz, *m*-CH, Ph], 6.99 [2H, t, J(H−H) = 8.0 Hz, *p*-CH, Ph], 5.12 (1H, s, CH), 1.03 [18H, s, C(CH_3)$_3$]. ^{13}C NMR: δ 182.0 (O$_2$$C$), 139.0 ($\alpha$-$C$, Ph), 129.6 (*m*-$C$H, Ph), 129.4 (*o*-$C$H, Ph), 128.5 (*p*-$C$H, Ph), 62 ($C$H), 30.0 [C($CH_3$)$_3$].

[(^{t}Bu)$_2$Al(μ-O$_2$CCPh$_3$)]$_2$ (6). This was prepared in a similar manner to compound **1**. Yield: 79%. Mp: 245 °C. Anal. Found (calc): Al, 6.1 ± 0.1 (6.3). MS (EI, %): *m/z* 799 ($M^+ -$ ^{t}Bu, 100), 742 ($M^+ -$ 2^{t}Bu, 10). IR (cm^{-1}): 3088 (w), 3027 (w), 3063 (w), 2935 (m), 2909 (m), 2829 (s), 2760 (w), 2740 (w), 2728 (w), 1955 (w), 1878 (w), 1807 (w), 1617 (w), 1492 (m), 1460 (m), 1417 (s), 1260 (m), 1193 (w), 1087 (m), 1036 (m). ^{1}H NMR: δ 7.49 [6H, d, J(H−H) = 8.0 Hz, *o*-CH, Ph], 7.15 [6H, dd, J(H−H) = 8.0 Hz, *m*-CH, Ph], 7.06 [3H, t, J(H−H) = 8.0 Hz, *p*-CH, Ph], 1.10 [9H, s, C(CH$_3$)$_3$]. ^{13}C NMR: δ 182.2 (O$_2$$C$), 132.0, 131.0, 129.0, 128.1 (C_6H$_5$), 30.4 [C(CH$_3$)$_3$].

[(^{t}Bu)$_2$Al{μ-O$_2$CC(H)=C(H)Ph}]$_2$ (7). This was prepared in a similar manner to compound **1**. Yield: 68%. Mp: 206 °C. Anal. Found (calc): Al, 9.7 ± 0.2 (9.4). IR (cm^{-1}): 2931 (s), 1921 (s), 1829 (s), 1640 (s), 1583(s), 1507 (m), 1447 (s), 1426 (s), 1261 (s), 1207 (m), 1180 (w), 1070 (w), 1027 (w), 1002 (m), 979 (m), 936 (w), 873 (m), 814 (m), 713 (m), 607 (m), 582 (m), 508 (m). ^{1}H NMR: δ 7.95 [1H, d, J(H−H) = 15 Hz, γ-CH], 7.02 (3H, m, *m*-, *p*-CH, Ph), 6.93 (2H, m, *o*-CH, Ph), 6.44 [1H, d, J(H−H) = 15 Hz, β-CH], 1.36 [18H, s, C(CH_3)$_3$]. ^{13}C NMR: δ 173.6 (O$_2$$C$), 150.8 ($\gamma$-$C$H), 133.5 ($C$, Ph), 131.9 (*p*-$C$H), 129.3 (*o*-$C$H), 129.2 (*m*-$C$H), 118.8 ($\beta$-C$H$), 29.9 [C($CH_3$)$_3$].

[(^{t}Bu)$_2$Al(μ-O$_2$CCH$_2$OCH$_3$)]$_2$ (8). HO$_2$CCH$_2$OCH$_3$ (0.91 mL, 11.0 mmol) was added to a toluene (50 mL) solution of Al(^{t}Bu)$_3$ (2.34 g, 11.0 mmol) at room temperature. Upon addition, the solution imediately became yellow and rapidly turned colorless. The reaction mixture was stirred overnight, and the volatiles were removed under vacuum. The solid was extracted with hexane (50 mL), filtered, concentrated, and cooled to −24 °C, to yield colorless crystals. Yield: 80%. Mp: 71 °C. Anal. Found (calc): Al, 10.9 ± 0.2 (11.7). MS (EI): *m/z* 403, 100% ($M^+ -$ ^{t}Bu). IR (neat): 2939 (s), 2931 (s), 2907 (s), 2888 (s), 2865 (s), 2827 (s), 1638 (s), 1500 (m), 1481 (m), 1463 (s), 1447 (m), 1342 (m), 1206 (m), 1132 (s), 1003 (w), 936 (w), 813 (m), 608 (m). ^{1}H NMR: δ 3.59 [4 H, s, O$_2$CCH_2], 2.93 (6 H, s, OCH_3), 1.17 [36 H, s, C(CH_3)$_3$]. ^{13}C NMR: δ 180.6 (O$_2$$C$), 70. 7 (O$_2CCH_2$), 59.0 (O$CH_3$), 29.8 [C($CH_3$)$_3$], 15.0 [$C$(CH$_3$)$_3$].

[(^{t}Bu)$_2$Al(μ-O$_2$CCH$_2$OCH$_2$CH$_2$OCH$_3$)]$_2$ (9). This was prepared in a similar manner to compound **8**. Yield: 65%. Mp: 43 °C. Anal. Found (calc): Al, 10.0 ± 0.2 (9.8). MS (EI): *m/z* 491, 35% ($M^+ -$ ^{t}Bu). IR (neat): 2967 (m), 2935 (s), 2922 (s), 2909 (s), 2889 (s), 2866 (s), 2832 (s), 2760 (w), 2727 (w), 2699 (w), 1630 (s), 1486 (s), 1462 (s), 1413 (m), 1381 (w), 1369 (m), 1359 (m), 1329 (m), 1300 (w), 1264 (w), 1239 (w), 1200 (m), 1156 (s), 1119 (s), 1033 (m), 1003 (m), 968 (w), 935 (w), 899 (w), 864 9w), 837 (w), 814 (s), 774 (w), 794 (w), 690 (m), 609 (s). ^{1}H NMR: δ 3.92 [4 H, s, O$_2$CCH_2], 3.35−3.20 [8 H, m, OCH_2CH_2], 3.04 [6 H, s, OCH$_3$], 1.18 [36 H, s, (CH_3)$_3$]. ^{13}C NMR: δ 180.6 [O$_2$$C$], 72.4, 71.0, 69.8 [$CH_2$], 58.7 [O$CH_3$], 29.9 [($CH_3$)$_3$C], 15.0 [(CH$_3$)$_3$$C$].

[(^{t}Bu)$_2$Al{μ-O$_2$CCH$_2$(OCH$_2$CH$_2$)$_2$OCH$_3$}]$_2$ (10). This was prepared in a similar manner to compound **8**. Yield: 70%. Mp: 45 °C. Anal. Found (calc): Al, 8.8 ± 0.2 (8.5). MS (EI): *m/z* 579 ($M^+ -$ ^{t}Bu, 35%), 261 [Al(^{t}Bu)MEEA, 100%]. IR (cm^{-1}): 2957 (s), 2923 (s), 2848 (s), 2828 (s), 1615 (s), 1505 (sh), 1470 (s), 1431 (w), 1356 (m), 1336 (m), 1243 (w), 1198 (m), 1110 (s), 1032 (m), 939 (w), 894 (m), 816 (m), 796 (w), 613 (m), 545 (w). ^{1}H NMR: δ 4.33 [2H, s, O$_2$CCH_2], 3.75, 3.66, 3.63, 3.52 (8H, m, OCH_2CH_2), 3.36 (3H, s, OCH_3), 0.849 [18H, s, C(CH_3)$_3$]. ^{13}C NMR: δ 179.8 (O$_2$$C$), 71.8, 71.1, 70.6, 69.7 (OCH$_2$$CH_2$), 58.9 (O$CH_3$), 29.3 [C($CH_3$)$_3$].

X-ray Crystallographic Studies. Crystals of [(^{t}Bu)$_2$Al(μ-O$_2$C^{t}Bu)]$_2$ (**1**), [(^{t}Bu)$_2$Al(μ-O$_2$CCH$_2$Ph)]$_2$ (**4**), and [(^{t}Bu)$_2$Al(μ-O$_2$CCH$_2$OCH$_2$CH$_2$OCH$_3$)]$_2$ (**9**) were sealed in a glass capillary under argon and mounted on the goniometer of a Enraf-Nonius CAD-4 automated diffractometer. Data collection and cell determinations were performed in a manner previously described.[49] The location of the majority of non-hydrogen atoms were obtained by using SIR,[50] while the remaining atomic coordinates were determined through the generation of dif-

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[49] Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.

Table 9. Summary of X-ray Diffraction Data

	compound			
	$[(^tBu)_2Al(\mu\text{-}O_2C^tBu)]_2$ (**1**)	$[(^tBu)_2Al(\mu\text{-}O_2CPh)]_2$ (**3**)	$[(^tBu)_2Al(\mu\text{-}O_2CCH_2Ph)]_2$ (**4**)	$[(^tBu)_2Al(\mu\text{-}O_2CCH_2\text{-}OCH_2CH_2OCH_3)]_2$ (**9**)
emp formula	$C_{26}H_{54}Al_2O_4$	$C_{30}H_{46}Al_2O_4$	$C_{32}H_{50}Al_2O_4$	$C_{26}H_{54}Al_2O_8$
cryst size, mm	0.14 × 0.16 × 0.21	0.40 × 0.22 × 0.62	0.32 × 0.34 × 0.39	0.11 × 0.12 × 0.14
cryst system	monoclinic	triclinic	triclinic	triclinic
space group	$C2/m$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	17.143(2)	8.397(7)	8.5051(9)	9.1043(8)
b, Å	12.098(1)	9.387(6)	10.1363(8)	10.790(1)
c, Å	8.7275(8)	11.033(5)	12.1121(8)	19.128(2)
α, deg		71.41(1)	66.600(6)	88.354(7)
β, deg	116.627(8)	75.230(9)	79.988(7)	81.580(7)
γ, deg		86.29(1)	66.903(7)	70.633(7)
V, Å^3	1618.1(3)	779.6(1)	881.3(1)	1753.2(3)
Z	2	1	1	2
D(calcd), g/cm^3	0.995	1.093	1.041	1.039
μ, mm^{-1}	1.09	0.121	1.07	1.14
radiation	Mo Kα (λ = 0.710 73 Å) graphite monochromator			
temp, K	298	298	298	298
2θ range, deg	4.0−50.0	4.0−40.0	2.0−44.0	3.0−44.0
no. collcd	2848	1596	2150	4295
no. ind	1503	1463	2150	4295
no. obsd	651 ($\|F_o\| > 6.0\sigma\|F_o\|$)	1330 ($\|F_o\| > 4.0\sigma\|F_o\|$)	1176 ($\|F_o\| > 6.0\sigma\|F_o\|$)	1060 ($\|F_o\| > 5.0\sigma\|F_o\|$)
weighting scheme	$w^{-1} = 0.04(\|F_o\|)^2 + \sigma(\|F_o\|)^2$	$w^{-1} = \sigma^2(\|F_o\|)$	$w^{-1} = 0.04(\|F_o\|)^2 + \sigma(\|F_o\|)^2$	$w^{-1} = 0.04(\|F_o\|)^2 + \sigma(\|F_o\|)^2$
R	0.0537	0.0468	0.0538	0.0478
R_w	0.0530	0.0468	0.0545	0.0622
largest diff peak, e Å^{-3}	0.09	0.20	0.21	0.24

ference Fourier maps using MolEN.[51] All hydrogen atoms were placed in calculated positions [d(C−H) = 0.95 Å, B(H) = 1.2B_{eq}(attached carbon)]. A summary of cell parameters, data collection, and structure solution is given in Table 9. Scattering factors were taken from ref 52.

A crystal of $[(^tBu)_2Al(\mu\text{-}O_2CPh)]_2$ (**3**) was mounted in glass capillary attached to the goniometer head of a Nicolet R3m/V four-circle diffractometer. Data collection unit cell and space group determination were all carried out in a manner previously described in detail.[53] The structures were solved using the direct methods program XS,[54] which readily revealed the positions of the Al, O, and the some of the C atoms. Subsequent difference Fourier maps revealed the position of all of the non-hydrogen atoms. All the organic hydrogen atoms were placed in calculated positions [U_{iso} = 0.08 Å^2; d(C−H) = 0.96 Å] for refinement. Neutral-atom scattering factors were taken from the usual source.[52] Refinement of positional and anisotropic thermal parameters led to convergence (see Table 9).

Computational Methods. In order to gain further understanding of the steric effects on the structure and relative stability of dialkylaluminum carboxylate dimers versus their unknown monomeric counterparts we have carried out *ab initio* calculations on a series of model compounds. *Ab initio* all electron molecular orbital (MO) calculations were performed using the GAUSSIAN 92[55] suite of programs. Initial optimization of all structures was carried out at the Hartree−Fock level with the STO-3G basis set. The results from these studies were used as the initial guess for optimization using the 3-21G(*) basis set.[56] To determine the relative energy of each species with electron correlation included, second-order Møller−Plesset (MP2) calculations were performed.[57]

Table 10. Structural Parameters for Planar $[H_2Al(\mu\text{-}O_2CH)]_2$ in Comparison to Experimental Values for $[(^tBu)_2Al(\mu\text{-}O_2C^tBu)]_2$ (1)[a]

	calcd			
param	HF/STO-3G	HF/3-21G(*)	HF/3-21G(*) fixed Al···Al[b]	exptl
Al−O	1.758	1.814	1.800	1.809(3)
Al−H	1.472	1.588	1.590	n/a
C−O	1.262	1.255	1.253	1.235(4)
C−H	1.114	1.074	1.072	n/a
Al···Al	4.392	4.522	4.296	4.296(3)
H−Al−H	124.8	122.7	123.3	124.1(2)[c]
O−Al−O	105.8	101.4	109.1	107.6(1)
H−Al−O	106.3	107.7	105.9	106.0(av)[d]
Al−O−C	153.1	156.9	153.7	155.1(3)
O−C−O	127.9	124.8	123.5	122.1(4)
O−C−H	116.0	117.6	118.3	118.9(2)[e]

[a] Distances in Å, angles in deg. [b] Al···Al distance fixed equal to the experimental value for $[(^tBu)_2Al(\mu\text{-}O_2C^tBu)]_2$. [c] C−Al−C. [d] C−Al−O. [e] O−C−C.

We have previously found the HF/3-21G(*) model to give good descriptions of the structures of organoaluminum compounds.[58] In this work we are seeking not the prediction of absolute structures but rather a qualitative explanation for observed structural features. In this regard, including the limit of computer time we do not feel the application of a larger basis set is warranted. However, in order to determine the relative ability of *ab initio* calculations at the HF/STO-3G and HF/3-21G(*) levels to simulate the observed crystallographic structures of aluminum carboxylate compounds, a series of geometry optimizations were carried out on the model compound $[H_2Al(\mu\text{-}O_2CH)]_2$ (**X**). To allow a direct comparison with an experimentally determined structure the $Al_2O_4C_2$ cycle was constrained to be planar, as is observed in the structure of $[(^tBu)_2Al(\mu\text{-}O_2C^tBu)]_2$ (**1**).

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The calculated structural and geometrical data for $[H_2Al(\mu-O_2CH)]_2$ at the HF/STO-3G and HF/3-21G(*) levels are given in Table 10 along with the appropriate values found from the X-ray structural determination of $[(^tBu)_2Al(\mu-O_2C^tBu)]_2$. As we have previously observed the calculated structure at the HF/3-21G(*) level is better at predicting the Al−O bond lengths and the bond lengths and angles associated with the carboxylate ligand. This is especially true if Al···Al is fixed to the experimentally determined value. In contrast, the values for the Al···Al distance and the bond angles around aluminum are better modeled at the HF/STO-3G level. On the basis of these results, the optimized geometries of monomeric aluminum compounds were determined at the HF/3-21G(*) level, while the structures of dimeric compounds were initially determined at the HF/STO-3G level to determine the Al···Al distances and subsequently re-optimized at the HF/3-21G(*) level with fixed Al···Al distances.

Acknowledgment. Financial support for this work is provided by the Office of Naval Research and the Robert A. Welch Foundation. The assistance of Dr. Terry Marriot (Rice University) with mass spectroscopic measurements is gratefully acknowledged.

Supporting Information Available: Full listings of atomic coordinates, bond lengths and angles, isotropic and anisotropic thermal parameters, and hydrogen atom parameters, tables of optimized structural parameters and energies for *ab initio* calculations, and ^1H and ^{13}C NMR spectra for compounds **1**−**10** (61 pages). Ordering information is given on any current masthead page.

OM960576Q