Synthesis and Properties of Calcium Tetraorganylalanates with $[Me_{4-n}AlPh_n]^-$ Anions

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Triphenylalane yields in THF or Et_2O the corresponding ether complexes $[(thf)AlPh_3]$ (**1a**) and $[(Et_2O)AlPh_3]$ (**1b**). The reaction of these triphenylalanes with phenylcalcium iodide in THF yielded quantitatively $[(thf)_5CaI][AlPh_4]$ (**2**), which can be recrystallized from diethyl ether/THF mixtures without ether exchange reactions. The reaction of $PhCa(thf)_4I$ with trimethylalane in THF in an equimolar ratio leads to the formation of solvent-separated $[(thf)_6Ca][AlMe_3Ph]_2$ (**5**), which immediately shows ligand redistribution. Therefore, a fractionated crystallization gives $[(thf)_6Ca][AlMe_2Ph_2]_2$ (**4**) at 4 °C, $[(thf)_4CaI_2]$ at −20 °C, and after reduction of the volume of the mother liquor $[(thf)_6Ca][AlMe_3Ph]_2$ (**5**) at −40 °C and $[(thf)_6Ca][AlMe_4]_2$ (**6**) at −78 °C. The formation of $(thf)_4CaI_2$ confirms that a Schlenk equilibrium is operative besides the ligand redistribution reactions. A solution of crystalline $[(thf)_6Ca][AlMe_2Ph_2]_2$ (**4**) in THF shows **4** as the major component besides $[(thf)_6Ca][AlMe_3Ph]_2$ (**5**) and $[(thf)_6Ca][AlMePh_3]_2$ (**3**). With an increasing number of methyl groups the melting points decrease from 210 °C for the tetraphenylalanate **2** to 20 °C for the tetramethylalanate **6**.

Introduction

Alanates have attracted the interest of many research groups for many decades, and the first review articles appeared already more than 40 years ago.[1,2] Recent review articles summarize the latest developments in this field.[3,4] On one hand, the formation of "ate" complexes of the type $M(M'R_n)$ with M being a more electropositive metal than M′ can lead to an increased reactivity compared to the starting homonuclear organometallics MR and $M'R_{n-1}$. Already in 1974, Chastrette and Gauthier reported that the "ate" complex $Ca(ZnR_4)$ is much more reactive toward ketones than either CaR_2 or ZnR_2.[5] On the other hand, lower reactivity was observed for $Li(AlPh_4)$ compared with phenyllithium and triphenylalane.[2] Wheras LiPh and $AlPh_3$ form triphenylmethanol with benzophenone, no reaction is observed between $Li(AlPh_4)$ and benzophenone. Already in 1913 triphenylalane, with a melting point of 196−200 °C, was prepared from $HgPh_2$ and Al chips in the absence of air and moisture.[6] A tetraphenylalanate was synthesized via the addition of phenyllithium to $AlPh_3$, yielding $[(Et_2O)_2Li][AlPh_4]$ or $[(thf)Li][AlPh_4]$ depending on the solvent.[7]

Calcium bis(tetraorganylalanates) have also been known for many decades. Lehmkuhl and Eisenbach prepared $Ca(AlEt_4)_2$ from $AlEt_3$ and calcium bis(alkoxides);[8] this pyrophoric calcium bisalanate showed nearly no conductivity and a surprising low melting point of 40 °C. Other synthetic procedures include the reaction of Ca, HgR'_2, and AlR_3 (R = Et, Pr, Ph; R′ = Et, Pr, Ph, Tol)[9,10] as well as the metathesis reaction of $CaCl_2$ with $Na(AlEt_4)$.[9] Transmetalation reactions of freshly prepared Ca turnings with $AlEt_3$ also offered a suitable access to $Ca(AlEt_4)_2$.[11,12] The reaction of $Ca(AlEt_4)_2$ (prepared from Ca, $HgPh_2$, and $AlEt_3$)[10] with benzophenone yielded at room temperature the Ph_2CO adduct, whereas at 90 °C in dodecane triphenylmethanol was formed.[13] From NMR experiments it was deduced that $Ca[AlEt_4]_2$ exists as an equilibrium between the ions $Ca^{2+}/2\ AlEt_4^-$ and the trinuclear molecule $[Ca\{(\mu\text{-}Et)_2AlEt_2\}_2]$.[14] Molecular $[R_2NCa(\mu\text{-}CH_2R)_2Al(CH_2R)_2]_2$ (R = $SiMe_3$) formed from the reaction of $[Ca(NR_2)_2]_2$ with $Al(CH_2R)_3$.[15] Incorporation of additional donor atoms supports the formation of molecular calcium bisalanates as shown for $[Ca\{(\mu\text{-}2\text{-}Py)_3AlMe\}_2]$ with a hexacoordinate calcium center.[16] Solvent-separated ions were obtained from the reaction of $(dme)_2Ca(NPh_2)_2$ and $AlMe_3$ in tetrahydrofuran, yielding $[(thf)_6Ca][Me_3AlNPh_2]^2$.[17]

The availability of phenylcalcium iodide,[18−22] our interest in heterobimetallic compounds,[4] and the interesting and unexpected properties of reported calcium bisalanates[1,2]

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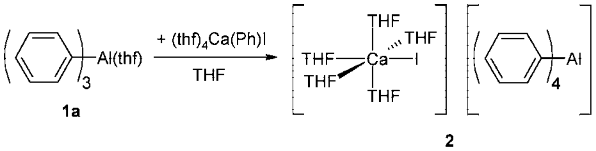
initiated our reinvestigation of calcium bisalanates of the type $[Ca(Me_{4-n}AlPh_n)_2]$[n = 4 (**2**), 3 (**3**), 2 (**4**), 1 (**5**), and 0 (**6**)]. For comparison reasons the molecular structures of $[(L)AlPh_3]$ (**1**) were determined. In the past only homoleptic alanate anions were prepared with one exception employing the reaction of Ca, HgR'_2, and AlR_3.[10]

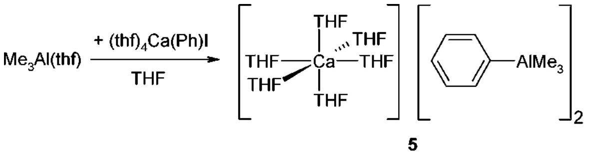
Results and Discussion

Synthesis. Triphenylalane was dissolved in THF or Et_2O, yielding the corresponding ether complexes $[(thf)AlPh_3]$ (**1a**) and $[(Et_2O)AlPh_3]$ (**1b**). The reaction of these organoaluminium compounds with phenylcalcium iodide in THF yielded quantitatively the tetraphenylalanates (eq 1). The solvent-separated ion pair $[(thf)_5CaI][AlPh_4]$ (**2**) can be recrystallized from diethyl ether/THF mixtures without ether exchange reactions. In order to investigate equilibriums in solution, heteroleptic alanates containing methyl and phenyl groups were synthesized.



(1)

The reaction of PhCa(thf)$_4$I with trimethylalane in THF in a stoichiometric ratio of 1:1 led to the formation of the solvent-separated addition product $[(thf)_6Ca][AlMe_3Ph]_2$ (**5**) (eq 2), which immediately shows a ligand redistribution. Therefore, other alanate anions were also present. A fractionated crystallization gave $[(thf)_6Ca][AlMe_2Ph_2]_2$ (**4**) at 4 °C. Further cooling of the mother liquor to −20 °C after removal of **4** led to precipitation of $[(thf)_4CaI_2]$. After reduction of the solvent and cooling to −40 °C $[(thf)_6Ca][AlMe_3Ph]_2$ (**5**) crystallized. Finally, cooling of the mother liquor to −78 °C afforded the precipitation of $[(thf)_6Ca][AlMe_4]_2$ (**6**). The formation and isolation of $(thf)_4CaI_2$ confirmed that a Schlenk equilibrium was operative in these solutions besides the ligand redistribution reactions.



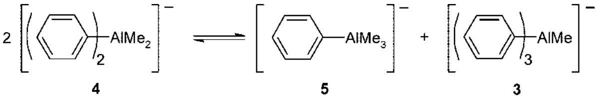
(2)

A solution of crystalline $[(thf)_6Ca][AlMe_2Ph_2]_2$ (**4**) in THF showed **4** as the major component; however, also minor amounts of $[(thf)_6Ca][AlMe_3Ph]_2$ (**5**) and $[(thf)_6Ca][AlMePh_3]_2$ (**3**) were present (eq 3). Thus, the whole series of calcium bisalanates of the type $[Ca(Me_{4-n}AlPh_n)_2]$ with n = 4 (**2**), 3 (**3**), 2 (**4**), 1 (**5**), and 0 (**6**) were obtained and investigated. With an increasing number of methyl groups the melting points decrease from 210 °C for the tetraphenylalanate **2** to 20 °C for the tetramethylalanate **6**. This low melting point for a calcium bis(tetralkylalanate) is in agreement with the findings of Lehmkuhl and Eisenbach.[8]

Table 1. $^{27}Al\{^1H\}$ **NMR Data (chemical shift** $\delta(^{27}Al)$ **and half-height width** $\omega_{1/2}$**) of the Alanate Anions of the Type** $[Me_{4-n}AlPh_n]^-$ [n **= 4 (2), 3 (3), 2 (4), 1 (5), and 0 (6)] ([D$_8$]THF solutions, 25°C)**[a]

alanate	compd	cation	$\delta(^{27}Al)$ (ppm)	$\omega_{1/2}$ (Hz)
$(AlPh_3)_2$			140	3700
$[(thf)AlPh_3]$	**1a**		148	3300
$[(Et_2O)AlPh_3]$	**1b**		147	3300
$[AlPh_4]^-$	**2**	$[(thf)_5CaI]^+$	132.9	31
$[AlMePh_3]^-$	**3**	$[(thf)_6Ca]^{2+}$	138.8	91
$[AlMe_2Ph_2]^-$	**4**	$[(thf)_6Ca]^{2+}$	144.6	91
$[AlMe_3Ph]^-$	**5**	$[(thf)_6Ca]^{2+}$	149.8	73
$[AlMe_4]^-$	**6**	$[(thf)_6Ca]^{2+}$	154.4	36

[a] For comparison reasons the parameters of $AlPh_3$ and its ether adducts are included as well.



(3)

$^{27}Al\{^1H\}$ NMR Spectroscopy. The $^{27}Al\{^1H\}$ NMR parameters of the compounds described above are summarized in Table 1. The chemical shift correlates with the coordination geometry of the complex and therefore indicates the coordination number of the aluminum centers in solution. Due to this fact, the chemical shifts of the $^{27}Al\{^1H\}$ resonances clearly lie in the characteristic range of 125−180 ppm for compounds with tetracoordinate aluminum atoms.[23−25] Due to the rather high symmetry, the half-height widths $\omega_{1/2}$ of the alanate anions are rather small, whereas the dimer $(AlPh_3)_2$ or the ether adducts of $AlPh_3$ show $\omega_{1/2}$ values of more than 3000 Hz. Furthermore, the half-height widths are dependent on the bulkiness of the substituents at aluminum.[24,25] The $^{27}Al\{^1H\}$ NMR experiments of $[(thf)_5CaI][AlPh_4]$ (**2**) showed a chemical shift of $\delta(^{27}Al)$ = 132.9 with a half-height width of only 31.3 Hz. In order to confirm that this compound consists of solvent-separated ion pairs in solution and that therefore the nature of the cation is irrelevant, $[Li(AlPh_4)]$ was prepared for comparison reasons and dissolved in DME and THF; this solution also showed a value of $\delta(^{27}Al)$ = 132.9 with a half-height width of 20 Hz and a coupling constant of $^1J(^{27}Al-^{13}C)$ = 94 Hz. The exchange of phenyl groups by methyl substituents leads to a gradual low-field shift of the $^{27}Al\{^1H\}$ NMR resonances of approximately 5 ppm. In Figure 1 the $^{27}Al\{^1H\}$ NMR spectra of [D$_8$]THF solutions of crystalline $[(thf)_6Ca][AlMe_2Ph_2]_2$ (**4**) and $[(thf)_6Ca][AlMe_3Ph]_2$ (**5**) are displayed. The relative intensities as shown in these spectra remain unchanged and indicate that an equilibrium between these species is operative.

Molecular Structures. For comparison reasons and in order to evaluate the influence of negative charge on the structural parameters of the alanates, the crystal structures of $[(thf)AlPh_3]$ (**1a**) (Figure 2) and $[(Et_2O)AlPh_3]$ (**1b**) were determined. The centrosymmetric dimer $Ph_2Al(\mu\text{-}Ph)_2AlPh_2$ contains three-center two-electron Al−C−Al bonds with a rather large average Al−C bond length of 2.182 Å, whereas the average Al−C distance of

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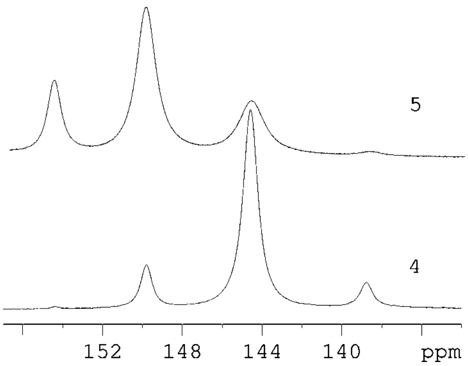

Figure 1. ^{27}Al{^{1}H} NMR spectra of [D$_8$]THF solutions of [(thf)$_6$Ca][Me$_3$AlPh]$_2$ (**5**) at the top and of [(thf)$_6$Ca][Me$_2$AlPh$_2$]$_2$ (**4**) at the bottom (25 °C, 104.28 MHz).

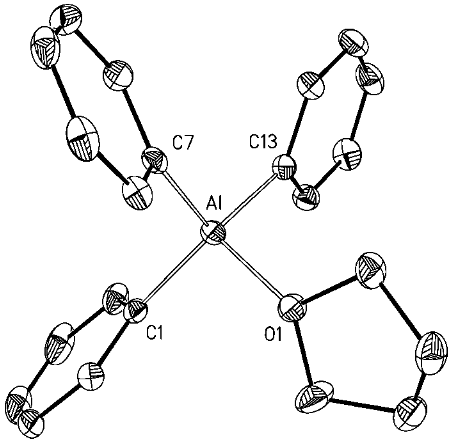

Figure 2. Molecular structure [(thf)AlPh$_3$] (**1a**). The ellipsoids represent a probability of 40%; H atoms are omitted for clarity reasons.

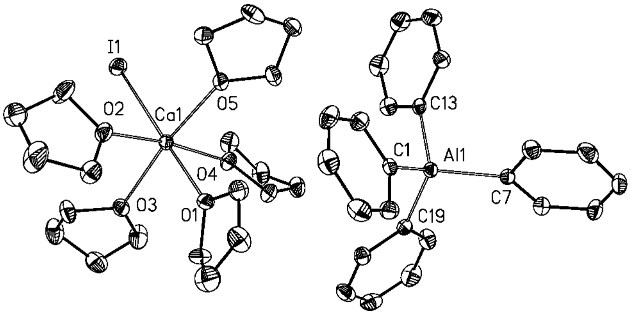

Figure 3. Molecular structure of [(thf)$_5$CaI][AlPh$_4$] (**2**). The ellipsoids represent a probability of 40%. The H atoms are omitted for clarity reasons.

Table 2. Selected Structural Parameters (bond lengths [Å], angles [deg]) of the THF and Et$_2$O adducts of AlPh$_3$ and of the Tetraorganylalanates [Me$_{4-n}$AlPh$_n$]$^-$ [n = 4 (2), 2 (4), and 1 (5)] of Calcium

	1a	**1b**	**2**	**4**	**5**
Al−C$_{Ph}$	1.976(2) 1.981(2) 1.982(2)	1.978(2) 1.984(2) 1.985(2)	2.006(4) 2.011(4) 2.017(4) 2.020(3)	2.029(3) 2.031(2)	2.021(2)
Al−C$_{Me}$				1.998(2) 2.003(3)	1.997(2) 1.999(2) 2.006(2)
Al−O	1.893(1)	1.920(1)			
O−Al−C$_{Ph}$^{a}	104.0	103.6			
C$_{Ph}$−Al−C$_{Ph}$^{a}	114.4	114.6	109.5	111.8(1)	
C$_{Me}$−Al−C$_{Me}$^{a}				114.9(1)	111.0
C$_{Ph}$−Al−C$_{Me}$^{a}				107.6	107.9
Ca−O^a			236.4	234.1	233.9
Ca−I			305.81(8)		

^{a} Average value if no esd is given.

the terminally bound phenyl groups shows a value of 1.958 Å.[26] The tetrahedral environment of the tetracoordinate aluminum atoms is distorted due to the small endocyclic C−Al−C bond angle of 103.5°. In the ether adducts **1a** and **1b** average Al−C bond lengths of 1.979 and 1.982 Å, respectively, are found. Comparable values were also published for the Et$_2$O adduct of tri(*o*-tolyl)alane (Al−C 1.998(3) Å, Al−O 1.928(3) Å)[27] and for the complex [Ph$_3$Al·P(SiMe$_3$)$_3$] (Al−C 1.990(5) Å, Al−P 2.514(2) Å).[28] The Al−O distances of the THF and diethyl ether adducts **1a** (Al−O1 1.893(1) Å) and **1b** (Al−O1 1.920(1) Å) differ slightly, in agreement with the larger basicity (e.g., Gutmann donor number)[29] of THF and the larger steric demand of Et$_2$O. In both complexes the C−Al−C bond angles are more than 10° larger than the O−Al−C values, in agreement with the VSEPR model.[30] Enhanced steric strain in [(thf)AlMes$_3$] (Mes = 2,4,6-trimethylphenyl, mesityl) leads to larger Al−O and Al−C distances of 1.969(5) and 2.017(7) Å, respectively.[31] These triaryl(tetrahydrofuran)alanes were successfully employed in catalytic arylation of aldehydes[32] and palladium-mediated cross-coupling reactions.[33]

Molecular structure and numbering scheme of [(thf)$_5$CaI][AlPh$_4$] (**2**) are represented in Figure 3. The [(thf)$_5$CaI] cation contains a hexacoordinate calcium atom in an octahedral environment. The Ca−I bond length of 3.0581(8) Å is smaller than that observed for (thf)$_4$CaI$_2$[34,35] and for (thf)$_4$Ca(Aryl)I[21,36] with hexacoordinate calcium atoms. Larger coordination numbers lead to larger Ca−I distances, as observed, for example, for (dme)$_2$(thf)CaI$_2$.[37] The average Ca−O distance of 2.364 Å in **2** lies in the characteristic range.

The tetraphenylalanate anion contains a tetrahedrally coordinated aluminum atom with an average Al−C bond length of 2.014 Å (Table 2). The elongation results from steric and electrostatic repulsion between the four phenyl anions. In the anion of [Cp$_2$Ta(CH$_2$)(Me)Al(C$_6$F$_5$)$_2$][Al(C$_6$F$_5$)$_4$] similar Al−C bond lengths of 2.016(2) Å were observed.[38] Despite different acceptor abilities of AlPh$_3$ and Al(C$_6$F$_5$)$_3$ (complexation energies

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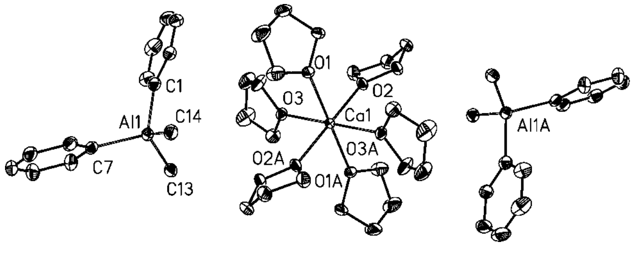

Figure 4. Molecular structure and numbering scheme of [(thf)$_6$Ca]-[Me$_2$AlPh$_2$]$_2$ (**4**). Symmetry-related atoms ($-x$, $-y$, $-z+1$) are marked with "A". The ellipsoids represent a probability of 40%. Hydrogen atoms are not shown for clarity reasons.

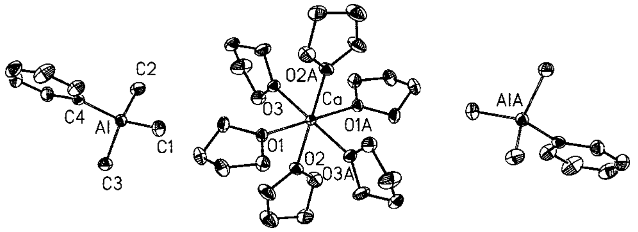

Figure 5. Molecular structure and numbering scheme of [(thf)$_6$Ca]-[Me$_3$AlPh]$_2$ (**4**). Symmetry-related atoms ($-x+1$, $-y$, $-z$) are marked with "A". The ellipsoids represent a probability of 40%. Hydrogen atoms are omitted for clarity reasons.

for $AlPh_3$ with H_2O and CH_3^- 63.8 and 401.1 kJ mol^{-1}, for $Al(C_6F_5)_3$ with H_2O and CH_3^- 112.0 and 521.5 kJ mol^{-1})[39] very similar bond lengths of the Al−C bonds in these alanate anions were observed and can be explained by steric repulsion. In the contact ion pair [Ca{(μ-2-Py)$_3$AlMe}$_2$] comparable Al−C distances (av value 2.021 Å) to the pyridyl moieties were found, whereas the Al−C$_{Me}$ distance showed a smaller value of 1.978(2) Å.[16]

Molecular structure and numbering scheme of [(thf)$_6$Ca]-[AlMe$_2$Ph$_2$]$_2$ (**4**) are displayed in Figure 4. The hexacoordinate calcium atom shows an average Ca−O distance of 2.341 Å. The Al−C bond lengths of the methyl groups (av Al−C$_{Me}$ 2.001 Å) of the dimethyldiphenylalanate anion are smaller than those of the phenyl substituents (av Al−C$_{Ph}$ 2.030 Å), which is in agreement of the observation at [Ca{(μ-2-Py)$_3$AlMe}$_2$].[16] In the contact ion pair [R$_2$NCa(μ-CH$_2$R)$_2$Al(CH$_2$R)$_2$]$_2$ (R = SiMe$_3$), average Al−C distances of 1.993 and 2.075 Å were found for the terminal and bridging trimethylsilylmethyl groups, respectively.[15]

Molecular structure and numbering scheme of [(thf)$_6$Ca]-[AlMe$_3$Ph]$_2$ (**5**) are shown in Figure 5. The distortions of the anion are as expected. The methyl groups cause slightly larger steric strain than phenyl groups, and therefore, the C$_{Me}$−Al−C$_{Me}$ bond angles are larger (av value 111.0°) than the average C$_{Me}$−Al−C$_{Ph}$ angle of 107.9°. The Al−C4 bond length of 2.021(2) Å to the phenyl substituent is also larger than the average Al−C$_{Me}$ value of 2.001 Å.

Summary

Alanates represent a compound class with enormous potential for applications in organic synthesis.[40] The calcium bis(tetraorganylalanates) of the type [Ca(Me$_{4-n}$AlPh$_n$)$_2$][n = 4 (**2**), 3 (**3**), 2 (**4**), 1 (**5**), and 0 (**6**)] are accessible via the addition of phenylcalcium iodide in THF to $AlPh_3$ (yielding **2**) or $AlMe_3$ (yielding **5**). The Schlenk equilibrium leads to the formation of (thf)$_4$CaI$_2$ and the calcium bisalanates, whereas due to the redistribution of the phenyl and methyl substituents all possible alanate anions (Me$_{4-n}$AlPh$_n$)$^-$ are observed. The ratio of phenyl to methyl groups strongly influences the melting point, leading to larger values for phenyl-rich alanates. All these calcium bis(alanates) form yellow solutions with THF, and even at elevated temperatures, no ether cleavage reactions are observed. This observation is in contrast to the "simple" phenylcalcium iodides, which cleave THF at rather low temperatures.[18−22,41] In the solid state and in solution, solvent-separated ions with tetrahedrally coordinated aluminum atoms are observed. In the ^{27}Al{^{1}H} NMR spectra a decreasing number of phenyl groups leads to a low-field shift of the resonances. In addition, the signals become narrower with a decreasing number of phenyl groups. However, the smallest half-height widths were observed for the homoleptic alanates [AlPh$_4$]$^-$ of **2** and [AlMe$_4$]$^-$ of **6**.

The tetraorganylalanate anions show only slightly distorted tetrahedrally coordinated aluminum atoms. The Al−C bond lengths are elongated compared to the neutral ether adducts of $AlPh_3$. The cations consist of calcium cations in octahedral environments. The Ca−O distances of [(thf)$_6$Ca]$^{2+}$ exhibit values around 2.34 Å, whereas the substitution of one THF ligand by an iodide anion leads to an elongation of the remaining Ca−O bonds of [(thf)$_5$CaI]$^+$ due to the reduced overall charge and, hence, reduced electrostatic attraction between Ca and O.

Experimental Section

General Remarks. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were dried according to common procedures and distilled under argon; deuterated solvents were dried over sodium, degassed, and saturated with argon. The ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on a Bruker AC 400 MHz spectrometer. ^{27}Al{^{1}H} NMR spectra were recorded on a Bruker Avance 400 at 104.27 MHz, and the spectra were externally referenced to a saturated [D$_8$]toluene solution of $AlCl_3$, at $\delta = 100.0$. Mass spectra were obtained on a Finnigan MAT SSQ 710 system, and IR measurements were carried out using a Perkin-Elmer System 2000 FTIR. The IR spectra were taken as Nujol mulls between KBr windows. Melting and decomposition points were measured with a Reichert-Jung apparatus type 302102 and are uncorrected. For the elemental analysis V_2O_5 was added to the samples in order to enhance combustion; nevertheless, carbon values are low most probably due to carbonate formation during combustion. $AlMe_3$ (2 M toluene solution) was purchased from Alfa Aesar. PhCaI(thf)$_4$,[21,22] Li(AlPh)$_4$,[7] [(thf)AlPh$_3$] (**1a**),[42] and [(Et$_2$O)AlPh$_3$] (**1b**)[43] were prepared according to literature procedures.

Synthesis of (Et$_2$O)AlPh$_3$ (1b) and AlPh$_3$. To a stirred suspension of $AlCl_3$ (74.98 mmol, 10.0 g; freshly sublimate) in Et_2O (50 mL) at −78 °C was slowly added a solution of PhLi (249.92 mmol, 142.0 mL, 1.76 M) in Et_2O. The mixture was stirred at −78 °C for 30 min and then allowed to warm to room temperature. The mixture was stirred for an additional 4 h and filtered. The volume of the filtrate was reduced to one-quarter and cooled to −40 °C. All solid materials were collected on a frit and extracted with toluene. Storage of the mother liquor at −40 °C led to precipitation of large colorless needles. Filtration and drying under vacuum at 50 °C yielded 11.23 g (33.78 mmol, 44%) of (Et$_2$O)AlPh$_3$ (**1b**).

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Table 3. Crystal Data and Refinement Details for the X-ray Structure Determinations of 1, 2, and 4

	1a	**1b**	**2**	**4**	**5**
formula	$C_{22}H_{23}AlO$	$C_{22}H_{25}Al\ O$	$C_{48}H_{68}Al\ CaIO_6$	$C_{52}H_{80}Al_2\ CaO_6$	$C_{56}H_{92}Al_2CaO_6$
fw ($g \cdot mol^{-1}$)	330.38	332.40	934.98	895.20	955.34
T/°C	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	9.5777(3)	12.1260(4)	9.5544(3)	12.8483(4)	12.5891(3)
b/Å	12.7810(6)	7.5520(3)	14.2629(5)	15.8241(5)	16.7864(3)
c/Å	16.0315(8)	21.1946(9)	19.1425(5)	12.9309(4)	13.8631(3)
α/deg	90.00	90.00	108.701(2)	90.00	90.00
β/deg	105.089(3)	100.231(3)	102.449(2)	90.000(3)	93.245(1)
γ/deg	90.00	90.00	92.823(2)	90.00	90.00
V/Å^3	1894.80(14)	1910.05(13)	2392.96(13)	2629.02(14)	2924.93(11)
Z	4	4	2	2	2
ρ ($g \cdot cm^{-3}$)	1.158	1.156	1.298	1.131	1.085
μ (cm^{-1})	1.12	1.11	8.39	1.97	1.81
no. measd data	12 581	13 073	16 920	18 456	20 524
no. data with $I > 2\sigma(I)$	2782	3125	7710	4009	5121
no. unique data/R_{int}	4312/0.0571	4352/0.0387	10 863/0.0331	6025/0.0535	6676/0.0373
wR_2 (all data, on F^2)[a]	0.1309	0.1238	0.1356	0.1461	0.1254
R_1 ($I > 2\sigma(I)$)[a]	0.0501	0.0470	0.0535	0.0550	0.0455
s[b]	1.020	1.015	0.961	1.031	0.992
res dens/e·Å^{-3}	0.245/−0.233	0.249/−0.209	1.172/−0.660	0.528/−0.510	0.490/−0.312
absorpt method	none	none	none	none	none
CCDC No.	690007	690008	690009	690010	690011

[a] Definition of the R indices: $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. [b] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

The solid was then dried under vacuum about 150 °C, extracted with boiling toluene, and filtered off. The extract was stored at −40 °C, and colorless needles were grown, which were collected and dried at 160 °C under vacuum for 2 h to yield 5.85 g of $AlPh_3$ (22.65 mmol, 30%).

Physical Data for 1b. Decomposition above 124 °C. Anal. Calcd for $C_{22}H_{25}AlO$ (332.42 g mol^{-1}): Al 8.11. Found: Al 7.92. ^1H NMR (200.13 MHz, 25 °C, [D$_6$]benzene): δ 1.13 (C*H*$_3$, Et$_2$O), 3.40 (C*H*$_2$, Et$_2$O), 7.20−7.28 (9H, m, *m*-H + *p*-H), 7.77 (6H, dd, *o*-H). $^{13}C\{^1H\}$ NMR (50.33 MHz, 25 °C, [D$_6$]benzene): δ 15.6 (*C*H$_3$, Et$_2$O), 66.2 (*C*H$_2$, Et$_2$O), 127.6 (6C, *m*-C), 127.9 (3C, *p*-C), 138.8 (6C, *o*-C), 148.4 (3C, *i*-C). ^{27}Al NMR (104.28 MHz, 25 °C, [D$_6$]benzene): δ 147.6 ($w_{1/2}$ = 3300 Hz). MS (EI, *m*/*z*, [%]): 39 (C_3H_3) [15], 78 (PhH) [100], 181 (M − Ph − Et$_2$O) [60], 255 (M − Ph) [30], 332 (M) [8]. IR (Nujol, KBr, cm^{-1}): 2924 vs (br), 1954 w, 1880 m, 1577 m, 1457 s, 1419 s, 1377 m, 1299 w, 1248 m, 1189 w, 1153 w, 1084 s, 1042 m, 1001 m, 994 m, 955 w, 919 m, 851 vs, 732 s, 706 vs, 680 vs, 473 vs, 453 m.

Physical Data for AlPh$_3$. Melting point 223 °C. Anal. Calcd for $C_{18}H_{15}Al$ (258.29 g mol^{-1}): Al 10.45. Found: Al 10.13. ^1H NMR (400.25 MHz, 25 °C, [D$_6$]benzene): δ 7.23 (3H, m, *m*-H, *p*-H), 7.76 (2H, dd, $^3J_{H-H}$ = 7.6 Hz, *o*-H). $^{13}C\{^1H\}$ NMR (100.65 MHz, 25 °C, [D$_6$]benzene): δ 127.6 (1C, *p*-C), 127.9 (2C, *m*-C), 138.8 (2C, *o*-C), 148.3 (1C, *i*-C). ^{27}Al NMR (104.28 MHz, 25 °C, [D$_6$]benzene): δ 140.3 ($w_{1/2}$ = 3700 Hz). MS (EI, *m*/*z*, [%]): 78 (PhH) [100], 104 (M − 2Ph) [24], 181 (M − Ph) [60], 258 (M) [40]. IR (Nujol, KBr, cm^{-1}): 2925 vs (br), 1958 w, 1889 w, 1836 w, 1774 w, 1595 w, 1578 m, 1465 vs, 1419 vs, 1388 s, 1377 s, 1323 m, 1283 w, 1246 m, 1192 m, 1148 m, 1086 vs, 1018 vs, 993 s, 888 s, 833 m, 722 vs, 728 vs, 704 vs, 680 vs.

Synthesis of (thf)AlPh$_3$ (1a). Solid AlPh$_3$ (0.18 g, 0.70 mmol) was dissolved in THF (5 mL) and stirred at room temperature for 1 h. Addition of Et$_2$O (5 mL) and cooling at −40 °C yielded large colorless needles, which were collected on a cooled frit and dried gently under vacuum to obtain 0.21 g of **1a** (0.64 mmol, 91%).

Physical Data for 1a. Mp: decomposition above 120 °C. Anal. Calcd for $C_{22}H_{23}AlO$ (330.41 g mol^{-1}): C 79.97, H 7.02, Al 8.17. Found: C 77.86, H 6.89, Al 7.58. ^1H NMR (200.13 MHz, 25 °C, [D$_8$]THF): δ 1.75 (C*H*$_2$, thf), 3.61 (C*H*$_2$O, thf), 7.23 (2H, t, $^3J_{H-H}$ = 6.6 Hz, *m*-H), 7.26 (1H, td, $^3J_{H-H}$ = 5.7 Hz, *p*-H), 7.76 (2H, dd, $^3J_{H-H}$ = 7.6 Hz, *o*-H). $^{13}C\{^1H\}$ NMR (50.33 MHz, 25 °C, [D$_8$]THF): δ 25.6 (*C*H$_2$, thf), 67.3 (*C*H$_2$O, thf), 127.7 (1C, *p*-C), 128.9 (2C, *m*-C), 138.8 (2C, *o*-C), 148.6 (1C, *i*-C). ^{27}Al NMR (104.28 MHz, 25 °C, [D$_6$]benzene): δ 147.6 ($w_{1/2}$ = 3300 Hz). MS (EI, *m*/*z*, [%]): 26 (C_2H_2) [80], 39 (C_3H_3) [70], 78 (PhH) [100], 176 (M − 2Ph) [10], 181 (M − Ph − thf) [8], 253 (M − Ph) [10]. IR (Nujol, KBr, cm^{-1}): 2924 vs (br), 1954 w, 1880 m, 1577 m, 1457 s, 1419 s, 1377 m, 1299 w, 1248 m, 1189 w, 1153 w; 1084 s, 1042 m, 1001 m, 994 m, 955 w, 919 m, 851 vs, 732 s, 706 vs, 680 vs, 473 vs, 453 m.

Synthesis of [(thf)$_5$CaI][AlPh$_4$] (2). Solid AlPh$_3$ (0.74 g, 2.86 mmol) was added in small portions within 30 min to a stirred solution of PhCaI(thf)$_4$ (33.0 mL, 2.87 mmol, 0.087 M) in THF at −40 °C. Then the reaction mixture was warmed to room temperature, stirred for additional 4 h, and filtered, and all volatiles were removed under vacuum. The solid residue was washed with 30 mL of toluene, dried under vacuum, and suspended in a mixture of 15 mL of Et$_2$O and 20 mL of THF. The solvent was reduced until the cloudy solution became clear. Storage at −40 °C led to the precipitation of colorless prisms, which were collected on a cooled frit and dried gently under vacuum, yielding 1.23 g of **2** (1.68 mmol, 59%). Decomposition above 210 °C. Anal. Calcd for $C_{44}H_{60}AlCaIO_5$ (862.91): C 61.24, H 7.01, Al 3.13, Ca 4,64. Found: C 59.08, H 7.18, Al 2.92, Ca 4.25. ^1H NMR (200.13 MHz, 25 °C, [D$_8$]THF): δ 1.74 (C*H*$_2$, thf), 3.56 (C*H*$_2$O, thf), 6.89 (1H, t, $^3J_{H-H}$ = 7.4 Hz, *p*-H), 7.05 (2H, t, $^3J_{H-H}$ = 7.3 Hz, *m*-H), 7.62 (2H, dd, $^3J_{H-H}$ = 7.4 Hz, *o*-H). $^{13}C\{^1H\}$ NMR (50.33 MHz, 25 °C, [D$_8$]THF): δ 26.3 (*C*H$_2$, thf), 68.2 (*C*H$_2$O, thf), 126.8 (1C, *p*-C), 128.9 (2C, *m*-C), 138.9 (2C, *o*-C), 139.8 (1C, *i*-C). ^{27}Al NMR (104.28 MHz, 25 °C, [D$_6$]benzene/[D$_8$]THF = 2:1): δ 132.9 ($w_{1/2}$ = 31 Hz). MS (FAB−, *m*/*z*, [%]): 335 (AlPh$_4$) [100]. MS (FAB+, *m*/*z*, [%]): 210 ((thf)CaI-CO) [100], 238 ((thf)CaI) [20], 257 ((thf)$_2$Ca) [23], 283 ((thf)$_2$CaI-CO) [50], 310 ((thf)$_2$CaI) [25], 527 ((thf)$_5$CaI) [3]. IR (Nujol, KBr, cm^{-1}): ν 3045 m, 2925 vs (br), 1459 s, 1417 m, 1377 m, 1244 w, 1180 w, 1075 m, 1023 s, 916 m, 870 m, 730 m, 706 s, 665 m, 475 m.

Synthesis of [(thf)$_6$Ca][AlMe$_2$Ph$_2$]$_2$ (4), [(thf)$_6$Ca][AlMe$_3$Ph]$_2$-(PhMe)$_2$ (5), and [(thf)$_6$Ca][AlMe$_4$]$_2$ (6). A 2 M solution of AlMe$_3$ in toluene (4.95 mL, 9.90 mmol, 2 M) was added dropwise to a solution of PhCaI(thf)$_4$ (30.0 mL, 9.90 mmol, 0.33 M) in THF at −78 °C and stirred for 30 min. Then the mixture was warmed to room temperature (at about −10 °C a clear solution formed) and stirred for an additional 12 h. Reduction of the volume of the reaction mixture to 20 mL, filtration, and storage of the yellowish solution at +4 °C led to precipitation of large colorless needles. Collection on a cooled frit and drying gently under vacuum gave 1.07 g of **4** (1.20 mmol, 24%). Storage of the mother liquor at −20 °C led to crystallization of 1.29 g of $(thf)_4CaI_2$ (2.22 mmol, 22%). After removal of this compound, the volume of the solution was reduced to 4.5 mL. Cooling of this mother liquor to −40 °C afforded the precipitation of 0.81 g (0.84 mmol, 19%) of **5**. Further cooling of the mother liquor at −78 °C led to formation of an amorphous white powder of **6** (0.26 g, 0.04 mmol, 1%). The yields refer to the amount of employed calcium.

Physical Data for 4. Mp: 53 °C (dec). Anal. Calcd for $C_{52}H_{80}Al_2CaO_6$ (895.23 g mol^{-1}): This compound is extremely air and moisture sensitive and loses coordinated THF once isolated. For this reason it was impossible to weigh out a definite amount because the weight of the substance changed permanently during handling and weighing in the glovebox. ^{1}H NMR (200.13 MHz, 25 °C, $[D_8]$THF): δ −0.94 (6H, s, Al−C*H*$_3$), 1.74 (C*H*$_2$, thf), 3.61 (C*H*$_2$O, thf), 6.80 (2H, t, $^3J_{H-H}$ = 6.8 Hz, *p*-H), 6.86 (4H, tt, $^3J_{H-H}$ = 7.6 Hz, *m*-H), 7.53 (2H, d, $^3J_{H-H}$ = 6.2 Hz, *o*-H). $^{13}C\{^1H\}$ NMR (50.33 MHz, 25 °C, $[D_8]$THF): δ −8.7 (2C, broad, Al-*C*H$_3$), 25.2 (*C*H$_2$, thf), 68.2 (*C*H$_2$O, thf), 123.9 (2C, *p*-C), 125.7 (4C, *m*-C), 138.7 (4C, *o*-C), 151.1 (2C, *i*-C). ^{27}Al NMR (104.28 MHz, 25 °C, $[D_8]$THF): δ 138.8 ($[AlMePh_3]^-$, $w_{1/2}$ = 91 Hz), 144.6 ($[AlMe_2Ph_2]^-$, $w_{1/2}$ = 91 Hz), 149.8 ($[AlMe_3Ph]^-$, $w_{1/2}$ = 73 Hz), 154.4 ($[AlMe_4]^-$, $w_{1/2}$ = 36 Hz). MS (FAB−, *m*/*z*, [%]): 211 ($AlMe_2Ph_2$) [10], 335 [100]. MS (FAB+, *m*/*z*, [%]): 210 [100], 257 ($(thf)_2Ca$) [22], 328 ($(thf)_4Ca$) [18], 372 ($(thf)_5Ca-C_2H_6$) [15]. IR (Nujol, KBr, cm^{-1}): 3040 m, 2923 vs (br), 1460 s, 1417 m, 1377 m, 1344 w, 1296 w, 1243 m, 1165 m, 1071 m, 1019 s, 918 m, 868 s, 733 m, 711 s, 674 s, 628 m, 612 m, 528 m, 464 w.

Physical Data for 5. Mp: 34 °C (dec). Anal. Calcd for $C_{56}H_{92}Al_2CaO_6$ (955.37 g mol^{-1}): This compound is extremely air and moisture sensitive and loses coordinated THF once isolated. For this reason it was impossible to weigh out a definite amount because the weight of the substance changed permanently during handling and weighing in the glovebox. ^{1}H NMR (200.13 MHz, 25 °C, $[D_6]$benzene/$[D_8]$THF (2:1)): δ −0.574 (18H, s, Al−C*H*$_3$), 1.72 (C*H*$_2$, thf), 2.29 (6H, s, C*H*$_3$ (toluene)), 3.69 (C*H*$_2$O, thf), 7.08−7.32 (14H, *m*-H + *p*-H + toluene), 7.98 (2H, d, *o*-H). $^{13}C\{^1H\}$ NMR (50.33 MHz, 25 °C, $[D_6]$benzene/$[D_8]$THF (2:1)): δ −8.8 (6C, broad, Al-*C*H$_3$), 21.5 (2C, *C*H$_3$ (toluene)), 25.6 (*C*H$_2$, thf), 68.7 (*C*H$_2$O, thf), 124.4 (2C, *p*-C), 126.1 (2C, C4 (toluene)), 126.3 (4C, *m*-C) 128.8 (4C, C3/5 (toluene)), 129,8 (4C, C2/6 (toluene)), 138.4 (2C, C1 (toluene)) 138.6 (2C, *o*-C), 151.2 (2C, *i*-C). ^{27}Al NMR (104.28 MHz, 25 °C, $[D_6]$benzene/$[D_8]$THF (2:1)): δ 138.8 ($[AlMePh_3]^-$, $w_{1/2}$ = 122 Hz), 144.7 ($[AlMe_2Ph_2]^-$, $w_{1/2}$ = 192 Hz), 150.1 ($[AlMe_3Ph]^-$, $w_{1/2}$ = 130 Hz), 154.7 ($[AlMe_4]^-$, $w_{1/2}$ = 104 Hz). MS (FAB−, *m*/*z*, [%]): 149 ($AlMe_3Ph$) [13]. IR (Nujol, KBr, cm^{-1}): 3039 m, 2923 vs (br), 2243 w, 2126 w, 1460 vs, 1377 s, 1296 w, 1243 w, 1166 m, 1102 m, 1071 m, 1018 s, 918 m, 870 m, 824 m, 710 s, 677 s, 628 m, 612 m.

Physical Data for 6. Mp: 20 °C (dec). Anal. Calcd for $C_{40}H_{96}Al_2CaO_6$ (646.95 g mol^{-1}): This compound is extremely air and moisture sensitive and loses coordinated THF once isolated. For this reason it was impossible to weigh out a definite amount because the weight of the substance changed permanently during handling and weighing in the glovebox. ^{1}H NMR (200.13 MHz, 25 °C, $[D_6]$benzene): δ −0.44 (24H, s, Al−C*H*$_3$), 1.32 (C*H*$_2$, thf), 3.53 (C*H*$_2$O, thf). $^{13}C\{^1H\}$ NMR (50.33 MHz, 25 °C, $[D_6]$benzene): δ −8.2 (8C, broad, Al-*C*H$_3$), 25.6 (*C*H$_2$, thf), 68.4 (*C*H$_2$O, thf). ^{27}Al NMR (104.28 MHz, 25 °C, $[D_6]$benzene): δ 155.0 ($[AlMe_4]^-$, $w_{1/2}$ = 125 Hz). IR (Nujol, KBr, cm^{-1}): 3040 w, 2923 vs, 2854 vs, 1460 s, 1417 w, 1377 m, 1296 w, 1243 w, 1165 w, 1071 m, 1028 s, 918 m, 874 s, 711 m, 674 m, 628 w, 612 w.

X-ray Structure Determinations. The intensity data for the compounds **1a**, **1b**, **2**, **4**, and **5** were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[44,45] The structures were solved by direct methods (SHELXS)[46] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97)[47] (Table 3). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[47] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

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Supporting Information Available: CIF files giving data collection and refinement details as well as positional coordinates of all atoms. This material is available free of charge via the Internet at http://pubs.acs.org. In addition, crystallographic data (excluding structure factors) has also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-690007 for **1a**, CCDC-690008 for **1b**, CCDC-690009 for **2**, CCDC-690010 for **4**, and CCDC-690011 for **5**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk].

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