Formation of Calcium–Carbon Bonds From a Lewis Acid-Base Reaction of Calcium Bis[bis(trimethylsilyl)amide] and Tris(trimethylsilylmethyl)alane

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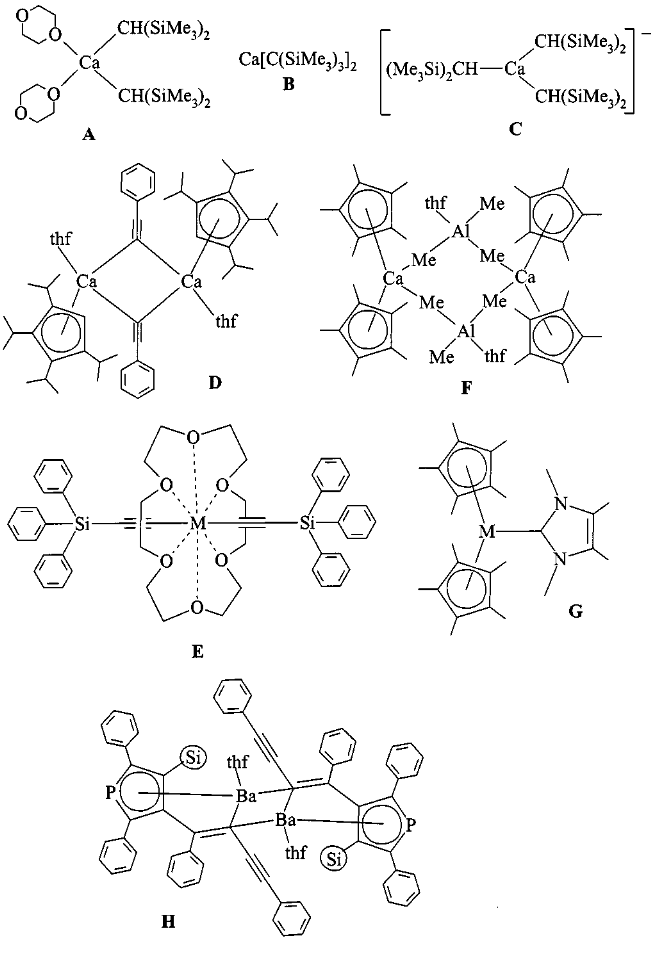
Treatment of calcium bis[bis(trimethylsilyl)amide] with two equivalents of tris(trimethylsilylmethyl)alane yields $(Me_3SiCH_2)_2Al–N(SiMe_3)_2$ (**1**) and the dimer $[(Me_3Si)_2N–Ca(\mu–CH_2SiMe_3)_2Al(CH_2SiMe_3)_2]_2$ (**2**). The five-coordinate bridging carbon atoms show Ca–C bond lengths of 264 and 268 pm. A similar reaction with calcium bis[bis(trimethylsilyl)phosphanide] gives the dimer $[(Me_3SiCH_2)_2Al–P(SiMe_3)_2]_2$ (**3**) with crystallographic $C2$ symmetry. A calcium-containing species is not isolable, however, in the presence of DME – ether cleavage reactions and the formation of the centrosymmetric dimer $[(Me_3SiCH_2)_2Al–OCH_2CH_2OMe]_2$ (**4**) are observed. The central moiety is an Al_2O_2 cycle with fivefold coordinated aluminium centers.

Introduction

In contrast to the well-developed chemistry of organo lithium compounds and the widely used Grignard reagents, only a few examples of compounds with σ-bonds between carbon and the heavier alkaline earth metals have been structurally characterized (Scheme 1). Several years ago Lappert and co-workers[1] reported the bis(1,4-dioxane) complex of bis[bis(trimethylsilyl)methyl] calcium **(A)** with Ca−C bond lengths of 248 pm. Solvent-free bis[tris(trimethylsilyl)methyl] calcium **(B)** crystallizes with a bent C−Ca−C moiety of 150° and Ca−C distances of 246 pm.[2] Compound **A** was prepared by a co-condensation reaction of calcium and bis(trimethylsilyl)methyl bromide. The metathesis reaction of $KC(SiMe_3)_3$ and calcium diiodide gave compound **B**. The reaction of alkaline earth metal arenesulfonates with bis(trimethylsilyl)methyl lithium or potassium yields alkali metal [tris(alkyl)alkaline earth metalates] **C**.[3] The metalation reaction is only applicable to organic substrates with acidic hydrogen atoms such as phenylacetylene as shown by Burkey and Hanusa[4] for the synthesis of $[(\eta^5\text{-}i\text{Pr}_4C_5H)Ca−C{\equiv}C−Ph]_2$ **(D)**. The crown ether complexes of the heavier alkaline earth metal bis(triphenylsilylacetylides) **E** display bent M−C≡C fragments.[5] The tetrahydrofuran complex of trimethylaluminium, which can act as a bridging ligand between the metal centers of decamethylcalcocene **F**, shows very long Ca−C distances of 295 and 300 pm.[6] Recently, the structures of the carbene complexes **G** were published by Arduengo and co-workers.[7] The dimeric barium compound **H** contains a central planar Ba_2C_2 cycle with Ba−C bond lengths of 288 and 307 pm.[8] In contrast to these rare examples of M−C σ-bonds numerous alkaline earth metallocenes have been reported.[9]



Scheme 1. Well-characterized molecules with alkaline earth metal−carbon σ-bonds (M = Ca, Sr, Ba); alkaline earth metallocenes and similar compounds are not considered

The reaction of trialkylalanes with alkaline earth metal bis(amides)[10] and bis(phosphanides)[10] seems to be an-

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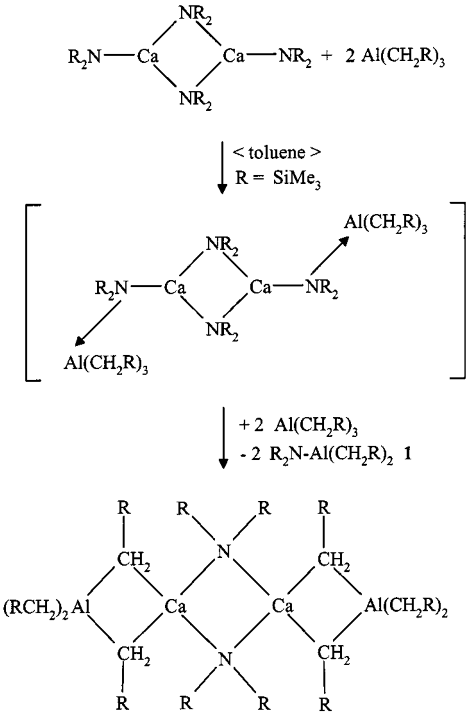
[+] X-ray structure analysis

other promising access to alkaline earth metal−carbon bonds. Magnesium bis(dialkylamide) reacts with trialkylaluminium to give the heteroleptic, dimeric alkylmagnesium dialkylamide and a dialkylamino dialkylalane.[11] Herein we report the results of the Lewis acid-base reaction between $Ca[E(SiMe_3)_2]_2$ (E = N, P) and tris(trimethylsilylmethyl)alane.

Results and Discussion

Synthesis

The addition reaction of tris(trimethylsilylmethyl)alane[12] and solvent-free calcium bis[bis(trimethylsilyl)amide][13] in a 2:1 molar ratio in toluene leads to a Lewis acid-base complex, although this compound could not be isolated. According to Equation 1 the elimination of bis(trimethylsilylmethyl)aluminium-bis(trimethylsilyl)amide **(1)** occurs spontaneously. Compound **1** can be removed from the reaction mixture in vacuo at elevated temperatures. Cooling of the concentrated reaction solution leads to the precipitation of crystalline dimeric calcium bis(trimethylsilyl)amide-tetrakis(trimethylsilylmethyl)aluminate **(2)**. The steric shielding of the central Ca_2N_2 cycle prevents another Lewis acid-base reaction even with a large excess of tris(trimethylsilylmethyl)alane in the reaction mixture. To allow the spectroscopic characterization of analytically pure compound **1** the metathesis reaction was performed with $[(Me_3SiCH_2)_2AlCl]_2$[14] and two equivalents of lithium bis(trimethylsilyl)amide according to Equation 2. The NMR spectra show three chemically different trimethylsilyl groups, which could be due to dimerization of **1**. However, in the mass spectrum the molecular ion of the monomer is the highest peak.



2

Equation 1. Synthesis of calcium aluminate **2**

$$(RCH_2)_2Al(\mu\text{-}Cl)_2Al(CH_2R)_2 + 2\,LiNR_2 \rightarrow 2\,(RCH_2)_2AlNR_2 + 2\,LiCl$$

R = SiMe$_3$ **1**

Equation 2. Synthesis of bis(trimethylsilylmethyl)aluminium bis(trimethylsilyl)amide **1**

Thus far, the use of calcium bis[bis(trimethylsilyl)phosphanide][10][15] as a synthon for the preparation of calcium−carbon bonds has failed. Solvent-free $Ca[P(SiMe_3)_2]_2$ is insoluble in aromatic and aliphatic hydrocarbons. The addition of $Al(CH_2SiMe_3)_3$ to a suspension of this calcium bis(phosphanide) in toluene leads to a clear solution. A $^{31}P\{^1H\}$ NMR spectroscopic investigation of the reaction reveals the formation of $[(Me_3SiCH_2)_2Al{-}P(SiMe_3)_2]_2$ **(3)**.[16] Nonetheless, an aluminate or a trimethylsilylmethyl calcium moiety could not be isolated. Compound **3** crystallizes from toluene and has a melting point of 218 °C, approximately 20 °C higher than reported by Wells and coworkers.[16] The spectroscopic data are consistent with a dimeric molecule of **3**. Performing this Lewis acid-base reaction in the presence of ethers such as tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) as solvents leads to an ether cleavage reaction. With DME, $[(Me_3SiCH_2)_2Al{-}OCH_2CH_2OMe]_2$ **(4)** with a central Al_2O_2 cycle was formed as one of the reaction products, although the isolation of an analytically pure product was not possible. The use of ether complexes and ether solutions seems to limit these Lewis acid-base reactions as a suitable pathway to calcium−carbon σ-bonds. The reactivity of alanes towards ethers has already been reported by Uhl[17] and Roesky.[18] Similar ether cleavage reactions have also been observed for bis[tris(trimethylsilyl)methyl] calcium **(B)**.[2] Treatment of **3** with DME also gives such reactions. Besides compound **4**, some unidentified substances were detected, although purification failed due to co-crystallization with side products.

Spectroscopic Characterization

The aluminate anion of **2** shows simple NMR spectra consistent with a free rotation. Even at temperatures of −70 °C it is not possible to halt the exchange process of the bridging and terminal trimethylsilylmethyl substituents. The negative charge leads to a high-field shift of the CH_2 group relative to compounds **1** and **3**. The $^{29}Si\{^1H\}$ NMR chemical shift ($\delta = -8.47$) of the bis(trimethylsilyl)amido ligand bridging the calcium atoms clearly proves that this complex remains dimeric in toluene solution. One would expect a value of approximately $\delta = -15$ for terminally bonded $(Me_3Si)_2N$ substituents[10][13] whereas a low-field shift of 6 to 8 ppm is characteristic of a bridging ligand with a quadruply coordinated nitrogen atom at calcium.

Molecular Structures

Compound **2** crystallizes in the monoclinic space group $P2_1/n$. Figure 1 shows the molecular structure and the numbering scheme. The bonding situation of the bridging trimethylsilylmethyl group with the freely refined hydrogen atoms is depicted in Figure 2. The central, planar Ca$_2$N$_2$ cycle with Ca1−N1 and Ca1−N1′ bond lengths of 240.7(2) and 248.7(2) pm, respectively, is slightly distorted although the values lie within the expected range.[10][13] The Ca1−C1 and Ca1−C2 distances [267.8(3) and 263.8(3) pm] are approximately 20 pm longer than in the above mentioned dialkyl calcium derivatives **A**[1] und **B**.[2] Similar values were obtained by Hanusa and co-workers[19] for bis[1,3-bis(trimethylsilyl)allyl]calcium. The bridging Me$_3$SiCH$_2$ substituents of **2** also show longer Al1−C distances [206.9(3) and 208.1(3) pm] compared to the terminal Al1−C3 and Al1−C4 bond lengths [198.9(3) and 199.7(3) pm]. The values for the terminal Al−C distances are in agreement with those in Al$_2$Me$_6$ [196(1) and 198(1) pm[20]] and are larger than in Al$_2$Ph$_6$ [195.6(5) and 196.0(5) pm[21]] as well as in Al2^{i}Pr6 [mean value 193(1) pm].[22] The rather large Ca−C distances and the short Al−C bonds to the bridging Me$_3$SiCH$_2$ groups in **2** compared to Al$_2$Me$_6$ [213(1) and 215(1) pm[20]] and Al$_2$Ph$_6$ [218.0(5) and 218.4(5) pm[21]] are a consequence of the distorted trigonal bipyramid coordination polyhedron of C1 and C2. The aluminium atom is located in the equatorial plane whereas the calcium atom is in an axial position. The other axial bonded group is the trimethylsilyl substituent. Therefore, the C1−Si1 and C2−Si2 bond lengths (mean value 189.6 pm) are elongated compared to C3−Si3 and C4−Si4 (mean value 185.2 pm).

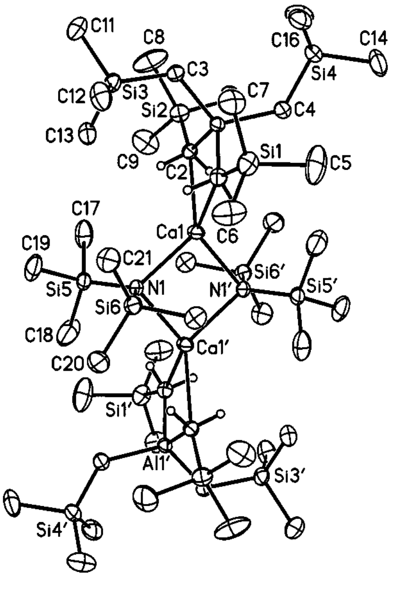


Figure 1. Molecular structure and numbering scheme of **2**; the ellipsoids represent a probability of 40%; hydrogen atoms with the exception of those at C1 and C2 are omitted for clarity reasons; symmetry-related atoms ($-x + 2$, $-y$, $-z$) are marked with an apostrophe; selected bond lengths (pm) and angles (°): Ca1−N1 240.7(2), Ca1−N1′ 248.7(2), Ca1−C1 267.8(3), Ca1−C2 263.8(3), Al1−C1 206.9(3), Al1−C2 208.1(3), Al1−C3 198.9(3), Al1−C4 199.7(3), C1−Si1 190.1(3), C2−Si2 189.2(3), C3−Si3 185.3(3), C4−Si4 185.0(3), N1−Si5 175.3(2), N1−Si6 174.1(2); N1−Ca1−N1′ 90.88(7), Ca1−C1−Al1 85.5(1), Ca1−C1−Si1 153.3(2), Al1−C1−Si1 117.8(2), Ca1−C2−Al1 86.3(1), Ca1−C2−Si2 154.2(1), Al1−C2−Si2 119.1(1), Al1−C3−Si3 123.6(2), Al1−C4−Si4 127.0(2)

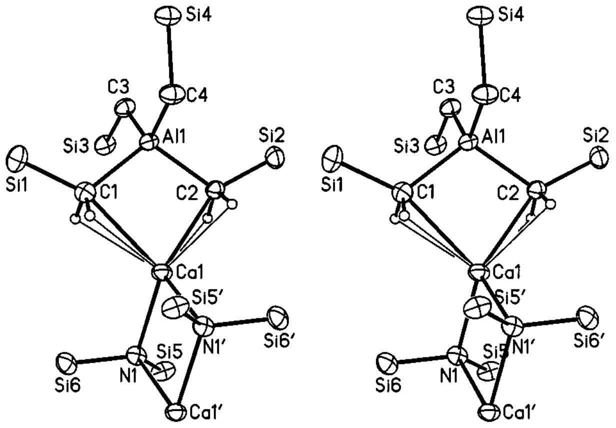


Figure 2. Stereoscopic representation of the coordination sphere at Ca1 of compound **2**; selected H-atoms are drawn with arbitrary radii, whereas all non-hydrogen atoms are represented on a 40% probability level; symmetry-related atoms ($-x + 2$, $-y$, $-z$) are marked with an apostrophe; the Ca−H interactions are represented by thin lines

The close contact Ca1···Al1 of 325.38(9) pm as well as the small bond angles Ca1−C1−Al1 and Ca1−C2−Al1 of 85.5(1)° and 86.3(1)°, respectively, can be described as two electron-three center bonds. On the other hand, an ionic arrangement with the calcium dication bonding to the C1−H as well as C2−H bonds (agostic interactions) could also explain the geometry of these bridging methylene fragments. As a consequence of these attractions small Ca1−C−H angles of between 57(2)° and 74(2)° as well as short Ca1···H contacts of between 232(3) and 258(3) pm are observed.

Figure 3 shows the molecular structure of **3**. Wells and co-workers[16] previously deduced the dimeric nature of **3** from NMR spectroscopic data. The Al1−P1 bond length of 248.0(1) pm is shorter than the Al−P distance of the adduct (Me$_3$SiCH$_2$)$_3$Al−P(SiMe$_3$)$_3$ [268.1(4) pm[16]] but in the same range as for (Me$_3$SiCH$_2$)$_2$Al(Br)−P(SiMe$_3$)$_3$ [249.8(7) pm[16]] and in the dimer [(Me$_3$SiCH$_2$)Al(Br)−P(SiMe$_3$)$_2$]$_2$ [243.6(2) pm[16]] with four-coordinate aluminium and phosphorus atoms. In comparison with the dimer with ethyl groups at the aluminium atom, the endocyclic bond lengths in **3** are elongated and a slight distortion is observed {[Et$_2$Al−P(SiMe$_3$)$_2$]$_2$: P−Al 246.0(1) and 245.4(1) pm, Al−P−Si: 114.21(5) and 114.46(5)°;[23] **3**: P−Al 248.0(1) and 248.6(1) pm, Al−P−Si: 112.07(4) and 115.93(5)°}.

The molecular structure of compound **4** is represented in Figure 4. The aluminium centers exhibit a trigonal bipyramidal geometry with the atoms O1′ and O2 in apical positions. Ring strain leads to a bent O1′−Al1−O2 geometry of 150.73(4)°. Due to the anionic charge on O1 (alcoholate oxygen), the Al1−O1 distance is smaller than the Al1−O2 distance [226.8(1) pm]. In agreement with the Gillespie−Nyholm rules the apical Al1−O1′ bond [190.3(1) pm] is slightly lengthened relative to the equatorial Al1−O1 bond [184.6(1) pm]. The Al−O distances lie in the range of known alkyl-substituted aluminium alkoxides obtained from ether cleavage reactions. There are a few reports of

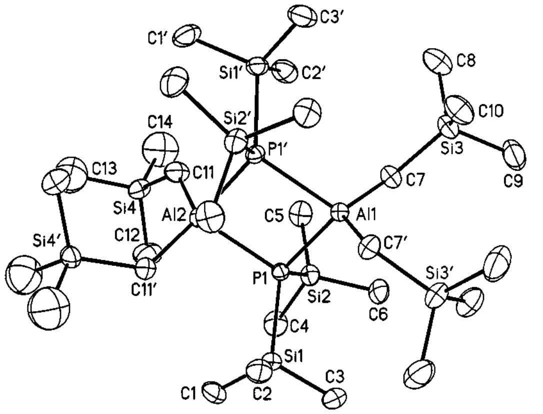


Figure 3. Molecular structure and numbering scheme of **3**: the ellipsoids are drawn at a 40% probability level and the hydrogen atoms omitted for clarity. Symmetry-related atoms ($-x$, y, $-z + 0.5$) are marked with an apostrophe; selected bond lengths (pm) and angles (°): P1−Al1 248.0(1), P1−Al2 248.6(1), P1−Si1 226.7(1), P1−Si2 226.8(1), Al1−C7 196.9(4), Al2−C11 196.3(4), C7−Si3 186.8(3), C11−Si4 183.6(3); Al1−P1−Al2 91.48(4), Si1−P1−Si2 104.55(5), C7−Al1−C7′ 119.6(2), C11−Al2−C11′ 121.9(2)

the cleavage of DME[17] and THF[18] during reduction of trimethylsilyl-substituted alkyl aluminium halides and the formation of the corresponding alkyl aluminium alcoholates. The Al1−C1 and Al1−C5 distances of 198.3(1) and 196.9(1) pm in **4** are similar to the values observed for **2**.

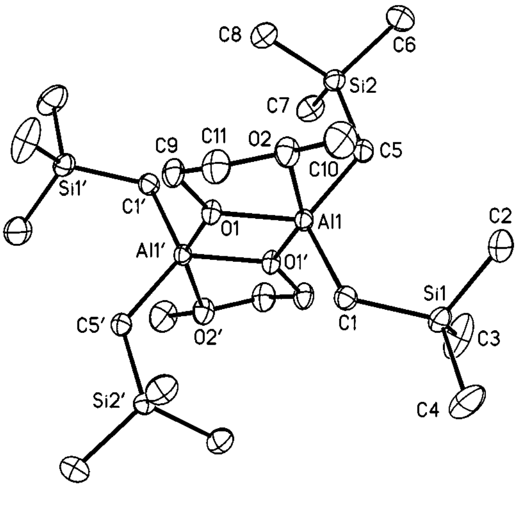


Figure 4. Molecular structure and numbering scheme of **4**; the ellipsoids represent a probability of 40%; the hydrogen atoms are omitted for clarity; symmetry-related atoms ($-x + 1$, $-y$, $--z$) are marked with an apostrophe; selected bond lengths (pm) and angles (°): Al1−O1 184.6(1), Al1−O1′ 190.3(1), Al1−O2 226.8(1), Al1−C1 198.3(1), Al1−C5 196.9(1); O1−Al1−O1′ 75.68(5), O1−Al1−O2 75.32(4), O1−Al1−C1 115.19(5), O1−Al1−C5 124.72(5), O1′−Al1−O2 150.73(4), O1′−Al1−C1 103.20(6), O1′−Al1−C5 103.69(6), O2−Al1−C1 92.59(6), O2−Al1−C5 89.67(6), C1−Al1−C5 118.43(6)

Conclusion

These experiments show that ether has to be excluded during the Lewis acid-base reactions of calcium bis(amides) and bis(phosphanides) with alanes. Furthermore, only calcium bis[bis(trimethylsilyl)amide] seems to be a valuable synthon for the strategy presented here because the heavier homologous phosphanides are insoluble in common organic solvents in the absence of ether. Thus far it has not been possible to eliminate another molecule of **1** from heteroleptic **2** to obtain bis(trimethylsilylmethyl)calcium

Experimental Section

General Remarks: All experiments and manipulations were carried out under argon or nitrogen purified by passage through BTS catalyst and P_4O_{10}. Reactions were performed with standard Schlenk techniques. All solvents were dried and thoroughly deoxygenated prior to use. The starting materials $Ca[N(SiMe_3)_2]_2$,[13] $(THF)_2Ca[P(SiMe_3)_2]_2$,[15] $ClAl(CH_2SiMe_3)_2$[14] and $Al(CH_2SiMe_3)_3$[12] were prepared according to literature procedures. NMR spectra were recorded on Jeol GSX270 and EX400 spectrometers. A Perkin−Elmer Paragon 1000 PC spectrophotometer was used to record the IR spectra; solid compounds were examined as Nujol mulls between CsBr plates (vs very strong, s strong, m medium strong, w weak, vw very weak, sh shoulder). The frequencies in the region of the Nujol vibrations are not listed. The low carbon values in the elemental analysis originate from carbide and carbonate formation during combustion of the compounds.

Bis(trimethylsilylmethyl)aluminium-bis(trimethylsilyl)amide (1). − Method 1: $Al(CH_2SiMe_3)_3$ (2.1 g; 8.96 mmol) was dropped slowly at 0 °C into a solution of calcium bis[bis(trimethylsilyl)amide] dimer (1.62 g, 2.24 mmol) in 25 mL of toluene. After complete addition, the solution was heated under reflux for five hours. Vacuum distillation yielded pyrophoric **1** (1.1 g, 1.52 mmol, 68%). The residue consisted mainly of compound **2**.

Method 2: At room temp. $ClAl(CH_2SiMe_3)_2$ (1.15 g, 4.87 mmol) was added to a solution of lithium bis(trimethylsilyl)amide (0.82 g, 4.88 mmol) dissolved in 12 mL of toluene. Colorless LiCl precipitated immediately. After heating for four hours at approximately 100 °C the NMR spectra showed a quantitative reaction. After removal of the solid materials vacuum distillation gave **1** (2.64 g, 3.65 mmol, 75%), b.p. 86 °C/0.15 Torr. − ^1H NMR ($[D_8]$toluene): $\delta = -0.51$ (broad) and -0.45 $[CH_2]$, 0.11 $[CSiMe_3]$, 0.13 and 0.18 $[NSiMe_3]$. − ^{13}C NMR ($[D_8]$toluene): $\delta = 2.40$ $[NSiMe_3$, $^1J(H-C) = 117.8$ Hz]. − $^{29}Si\{^1H\}$ NMR ($[D_8]$toluene): $\delta = -0.24$ and -2.50, 0.11. − IR: $\tilde{\nu} = 2953$ vs, 2901 m, 1647 vw, 1616 vw, 1587 vw, 1436 w, 1408 w, 1346 vw, 1250 vs, 1182 m, 1133 vw, 1056 m, 985 m, 934 s, 915 s, 887 s, 839 vs, 750 s, 682 m, 618 m, 575 m cm^{-1}. − MS (70 eV); m/z (%): 362 (3)$[M^+]$, 347 (9)$[M^+ - Me]$, 274 (70)$[Me_9Si_3CH_2AlN^+$ or $Me_9Si_3(CH_2)_2Al^+]$, 201 (85)-$[Me_6Si_2CH_2AlN^+$ or $Me_6Si_2(CH_2)_2Al^+]$, 160 (93) $[NSi_2Me_6{}^+]$, 146 (100), 128 (100) $[Me_3SiCH_2AlN^+]$. − $C_{14}H_{40}AlNSi_4$ (361.81): calcd. C 46.47, H 11.14, N 3.87; found C 45.48, H 11.15, N 3.55.

Calcium Bis(trimethylsilyl)amide-tetrakis(trimethylsilylmethyl)aluminate (2): At 0 °C tris(trimethylsilylmethyl)alane (2.4 g, 10.32 mmol) was added slowly to a solution of dimeric calcium bis[bis(trimethylsilyl)amide] (1.92 g, 2.67 mmol) in 25 mL of toluene. This solution was stirred at room temp. for an additional four days. During this time the solution turned slightly cloudy. After evaporation of solvent to 15 mL colorless crystals of **2** (1.1 g, 0.95 mmol, 36%) precipitated at 0 °C, m.p. 81 °C (dec.). − ^1H NMR ($[D_8]$toluene): $\delta = -0.89$ $[CH_2]$, 0.27 $[NSiMe_3]$, 0.28 $[CSiMe_3]$. − $^{13}C\{^1H\}$ NMR ($[D_8]$toluene): $\delta = 3.04$ $[CSi\mathit{Me}_3]$, 5.53 $[NSi\mathit{Me}_3]$, 10.09 $[\mathit{C}H_2]$. − $^{29}Si\{^1H\}$ NMR ($[D_8]$toluene): $\delta = -8.47$ $[NSiMe_3]$, 2.07

Table 1. Crystallographic data for **2, 3** and **4** as well as details of the structure solution and refinement procedures[a]

Compound	**2**	**3**	**4**
formula	$C_{22}H_{62}AlCaNSi_6$	$C_{28}H_{80}Al_2P_2Si_8$	$C_{22}H_{58}Al_2O_4Si_4$
fw [$g\cdot mol^{-1}$]	576.33	757.54	553.00
T [K]	173(2)	193(2)	183(2)
space group[26]	$P2_1/n$	*P*bcn (no. 60)	*P*1bar (no. 2)
a [pm]	1284.63(3)	1263.4(4)	920.38(2)
b [pm]	1666.51(3)	2084.8(6)	984.26(2)
c [pm]	1732.20(2)	1842.1(4)	1025.55(1)
α [°]	90	90	71.615(1)
β [°]	94.780(1)	90	88.770(1)
γ [°]	90	90	78.804(1)
V [nm^3]	3695.5(1)	4852(2)	864.05(3)
Z	4	4	1
d_{calcd} [$g\cdot cm^3$]	1.036	1.037	1.063
μ [mm^{-1}]	0.399	0.340	0.245
$F(000)$	1272	1664	304
scan range [°]	$13.62<2\theta<50.70$	$13.66<2\theta<46.52$	$4.18<2\theta<57.76$
measured data	18228	16721	5067
unique data (R_{int})	5919 (0.0419)	2674 (0.0245)	2729(0.0142)
absorption. corr.	none	semi-empirical	semi-empirical
max./min. transmission		0.694/0.594	0.9526/0.8873
parameters	330	194	152
restraints	0	12	0
wR_2[a] (all data, on F^2)	0.0953	0.1089	0.0769
R_1[a] (all data)	0.0660	0.0467	0.0317
data with $I > 2\sigma(I)$	4820	2430	2443
R_1 [$I > 2\sigma(I)$]	0.0470	0.0414	0.0275
goof s[b] on F^2	1.169	1.094	1.071
residual dens. [$e\cdot nm^{-3}$]	0.270/-0.199	0.578/-0.314	0.273/-0.180

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

[$CSiMe_3$]. − IR (nujol): ṽ = 1599 w, 1561 vw, 1405 w, 1345 vw, 1295 sh, 1247 vs, 1181 w, 960 vs, 933 s, 883 vs, 855 vs, 828 vs, 785 m, 754 s, 694 m, 681 m, 640 w, 617 w, 604 w, 587 m, 578 m, 538 w, 519 w, 491 vw, 450 w, 422 w, 404 w, 362 w, 330 vw, 306 w cm^{-1}. − $C_{44}H_{124}Al_2Ca_2N_2Si_{12}$ (1152.66): calcd. C 45.85, H 10.84, N 2.43; found C 43.45, H 10.33, N 2.59.

Bis(trimethylsilylmethyl)aluminium-bis(trimethylsilyl)phosphanide (3): To a solution of magnesium bis[bis(trimethylsilyl)phosphanide] (1.00 g, 2.65 mmol) in 20 mL of toluene $Al(CH_2SiMe_3)_3$ (2.4 g, 10.32 mmol) was added slowly at room temp. After stirring for 48 hours the solution was reduced in volume to 12 mL. At −15 °C colorless crystals of **3** (1.4 g, 1.85 mmol, 70%) precipitated, m.p. 218 °C. − ^1H NMR ([D_8]toluene): δ = −0.21 [CH_2, $^3J(H-P)$ = 2.6 Hz], 0.33 [$CSiMe_3$], 0.48 [$PSiMe_3$, $^3J(H-P)$ = 2.4 Hz]. − $^{13}C\{^1H\}$ NMR ([D_8]toluene): δ = 2.18 [CH_2], 3.82 [$CSiMe_3$], 4.98 [$PSiMe_3$, $|^1J(C-P) + {}^3J(C-P)|$ = 8.4 Hz]. − $^{29}Si\{^1H\}$ NMR ([D_8]toluene): δ = 0.23 [$CSiMe_3$, $^3J(Si-P)$ = 3.4 Hz], 6.38 [$PSiMe_3$, $|^1J(Si-P) + {}^3J(Si-P)|$ = 6.2 Hz]. − $^{31}P\{^1H\}$ NMR ([D_8]toluene): δ = −231.49. − IR (nujol): ṽ = 1439 w, 1401 w, 1348 w, 1312 w, 1242 s, 964 s, 941 m, 854 vs, 838 vs, 826 vs, 754 s, 747 s, 685 m, 639 m, 626 m, 559 m, 525 m, 446 m, 422 m, 360 m, 320 vw, 285 w cm^{-1}. − MS (70 eV, selected peaks); m/z (%): 596 (7) [$Al_2P_2Si_7Me_{21}^+$], 468 (35) [$(Me_3Si)_4P_2AlCH_2SiMe_3^+$], 378 (100) [$(Me_3Si)_2PAlCH_2SiMe_3^+$]. This compound has already been described by Wells and co-workers,[16] however, the spectroscopic data differ slightly.

X-ray Structure Determinations of 2, 3 and 4:[24] The single crystals were covered with nujol[25] and mounted on a Siemens P4 diffractometer with graphite monochromated Mo-K_α radiation (λ = 71.073 pm). A Siemens SMART−CCD area detector was used to monitor the reflections. Crystallographic parameters and details of data collection are summarized in Table 1. All structures were solved by direct methods and refined with the software packages SHELXL-93 and SHELXL-97.[27] Neutral scattering factors were taken from Cromer and Mann[28] and for the hydrogen atoms from Stewart et al.[29] The non-hydrogen atoms were refined anisotropically. The H-atoms were considered with a riding model under restriction of ideal symmetry at the corresponding atom.

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[24] Crystallographic data (excluding structure factors) for the structures of **2**, **3**, and **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-122179 for **2**, -122180 for **3**, and -122181 for **4**. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
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