

Synthesis and derivatization of naphthylcalcium halides as well as degradation in THF solution

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Abstract

The direct synthesis of 1-naphthyl iodide and -bromide with calcium powder yields $(\text{thf})_4\text{Ca}(\text{Naph})\text{I}$ (**1**) and $[(\text{thf})_3\text{Ca}(\text{Naph})\text{Br}]_2$ (**2**), respectively. The metathesis reaction of **1** with $\text{KN}(\text{SiMe}_3)_2$ gives $(\text{thf})_3\text{Ca}(\text{Naph})\text{N}(\text{SiMe}_3)_2$ (**3**). In **2** and **3** very small Ca–C bond lengths of 252.8(4) and 251.4(6) pm, respectively, are observed. These compounds slowly decompose in THF solution via ether cleavage reactions. From this degradation, $[(\text{thf})_4\text{CaBr}_2] \cdot \text{naphthalene}$ (**4**) crystallizes from THF solutions. Furthermore, decomposition of **1** in THF solution yields ethene and naphthalene whereas intermediate ethenolate undergoes subsequent degradation to an acetylide.

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1. Introduction

Arylcalcium compounds are becoming routinely available by direct synthesis of activated calcium with aryl halides [1–3]. Phenylcalcium iodide was already prepared more than a hundred years ago by Beckmann who described phenylcalcium iodide as a sparingly soluble solid [4]. Thereafter, Gilman and Schulze [5] repeated the synthesis of alkyl- and phenylcalcium halides and observed that not the organometallic compound precipitated but the ether complex of calcium dihalide. Many years later, larger aromatic systems such as naphthylcalcium halides and degradation reactions in THF were included in these studies by Bryce-Smith and Skinner [6]. Naphthylcalcium iodide prepared from naphthyl iodide and calcium could be stabilized by coordination of ethers such as 1,4-dioxane and THF [7]. In order to raise the yield, Mochida and coworkers investi-

gated the reaction of ultrafine calcium particles with naphthyl halides and the cocondensation reaction of calcium vapour with THF and aryl halides. The ultrafine Ca particles reacted with naphthylbromide, however, no reaction occurred with naphthylchloride [8]. The cocondensation of calcium with THF and naphthylhalide gave higher yields for the bromide, low yields of naphthylcalcium chloride were deduced from derivatization reactions [9]. However, codeposition of calcium atoms and dimethylether showed that calcium atoms are reactive enough to undergo side-reactions with ethers [10]. Halide-free dinaphthylcalcium was obtained from the transmetallation reaction of dinaphthylmercury with calcium shavings [11–13]. All these naphthylcalcium derivatives were identified via derivatization reactions with e.g. water, ketones, aldehydes. However, no physical data or molecular structures of these naphthylcalcium halides were reported.

The reaction of naphthyl halide with calcium is also interesting with respect to reduction of the π -system. The reaction of calcium with anthracene was employed in order to activate the alkaline earth metal [14]. Recently, the complex of naphthalene with calcium was studied with quantum

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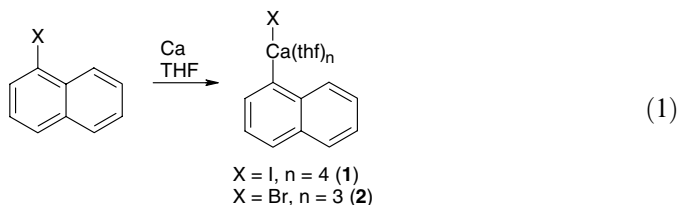
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chemical methods [15]. However, during the reduction of naphthyl halides with calcium in ether solvents a π -complex was never observed.

In solution, THF complexes of heteroleptic organylcalcium halides can show two possible reaction pathways: (i) Redistribution of the anionic ligands, known as Schlenk equilibrium, yields homoleptic diorganylcalcium and calcium dihalide. (ii) Aggregation of organylcalcium halides could proceed via a bridging halide or via a bridging organyl group after liberation of THF from the coordination sphere. Quantum chemical investigations at phenylcalcium iodide showed that aggregation of phenylcalcium iodide could occur via the phenyl groups which show a σ -bond to one Ca atom and a η^6 -coordination to the π -system for the other calcium atom [16]. Furthermore, bridging phenyl groups as in $[\text{ICa}(\mu\text{-Ph})_2\text{CaI}]$ are energetically favoured compared to bridging iodide ions as in $[\text{PhCa}(\mu\text{-I})_2\text{CaPh}]$. Recently, the reaction of activated calcium with naphthyl iodide yielded the monomeric tetrakis(THF) complex of naphthylcalcium iodide with a Ca–C bond length of 255.2(6) pm [17]. However, neither a Schlenk equilibrium nor aggregation or oligomerization was observed in THF solution. Here, we present our results on the synthesis of naphthylcalcium halides and a comparison with the properties of the phenylcalcium derivatives.

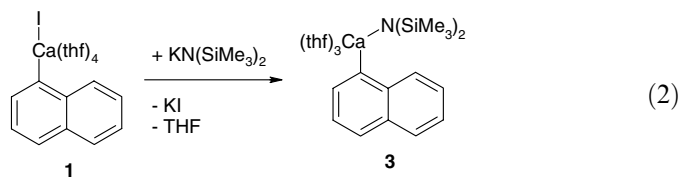
2. Results and discussion

The direct synthesis of naphthylcalcium iodide (**1**) from activated calcium with iodo naphthalene succeeded smoothly according to Eq. (1) [17]. The yield of naphthylcalcium bromide (**2**) was satisfactory, whereas chloro naphthalene did not react with activated calcium in THF. NMR spectroscopic investigations showed that **2** crystallized as a tris(THF) complex whereas **1** contained four THF molecules.



The metathesis reaction of tetrakis(tetrahydrofuran) naphthylcalcium iodide (**1**) with potassium bis(trimethylsilyl)amide yielded tris(tetrahydrofuran) naphthylcalcium bis(trimethylsilyl)amide (**3**) in analogy to the reaction of $(\text{thf})_4\text{Ca}(\text{Ph})\text{I}$ with $\text{KN}(\text{SiMe}_3)_2$ [18]. The substitution of the halide anion by the bulky amido group led the reduction of the number of coordinated THF molecules. Despite the bulkiness of the amido ligand, compound **3** decomposed much faster in THF solution than the arylcalcium halides **1** and **2**. Within 20 days, **3** disappeared completely and the NMR spectra showed only naphtha-

lene and ethane, which can be explained by THF cleavage reactions, as well as bis(tetrahydrofuran)calcium bis[bis(trimethylsilyl)amide].



The naphthylcalcium halides slowly decomposed in THF solution. After isolation of crystalline **2**, the mother liquor was stored for two weeks at -90°C . During this time colorless crystals formed which consisted of $[(\text{thf})_4\text{CaBr}_2] \cdot \text{naphthalene}$ (**4**). Naphthalene stems from α -deprotonation of THF by naphthylcalcium bromide whereas the formation of calcium dibromide occurs in course of the THF degradation, however, a Schlenk equilibrium was not observed. THF cleavage reactions should also yield ethenolate which was neither observed in the NMR spectra nor as a precipitate.

In order to investigate the products of the THF cleavage reaction, the THF solution of naphthylcalcium iodide was stored at room temperature for 30 days. Thereafter, the reaction mixture was quenched with chloro-trimethylsilane. Thereafter, the products were separated via gas chromatography (Fig. 1). The main products were naphthalene and trimethylsilylnaphthalene. A third product was bis(trimethylsilyl)acetylene which has to be interpreted as the degradation product of the ethenolate. A reasonable reaction sequence is proposed in Eq. (3), neglecting coordinated THF ligands.

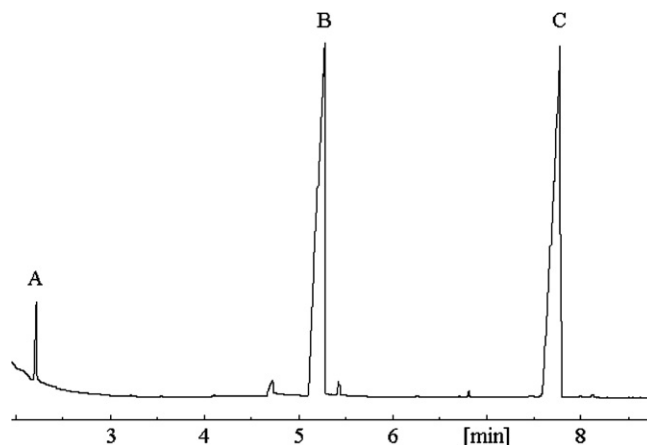
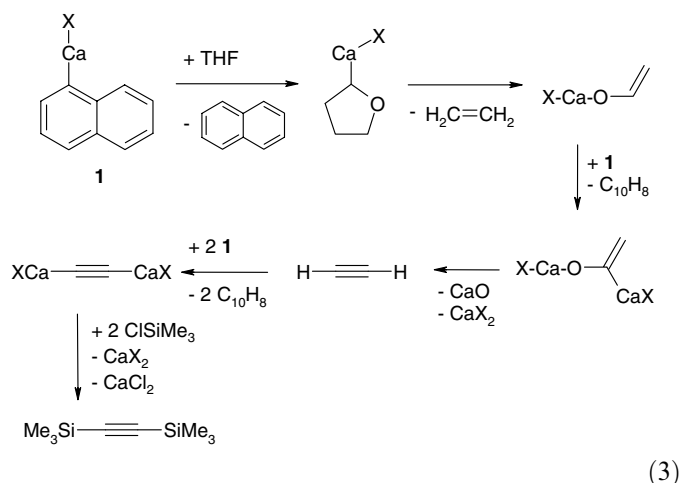


Fig. 1. Chromatogram of the products, obtained from THF degradation of $(\text{thf})_4\text{Ca}(\text{Naph})\text{I}$ in THF after 30 days and subsequent quenching of the reaction mixture with ClSiMe_3 . The signals were assigned to $\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{SiMe}_3$ (A), naphthalene (B) and $\text{Naph}-\text{SiMe}_3$ (C) (see text). Conditions: column CP-Sil5CB (25 m, diameter 0.25 mm, methylsilicone); carrier gas: H_2 , 2 mL min^{-1} ; temperature starting at 20°C and raising with $20^\circ\text{C min}^{-1}$, FID detector.



The first reaction step is the α -deprotonation of a THF molecule with a subsequent cleavage to ethene and ethenolate. Deprotonation of the ethenolate with **1** would occur again in α -position as was shown for the metallation reaction of ethyl vinyl ether with *tert*-butyllithium [19]. The resulting compound can be considered as a carbenoid which would liberate calcium dihalide and calcium oxide yielding acetylene after a hydrogen migration. It was already shown that calcium oxide often was trapped via addition of arylcalcium compounds giving for example $[(\text{thf})_2\text{CaPhI}]_3 \cdot (\text{thf})\text{CaO}$ [20] from THF cleavage with $(\text{thf})_4\text{CaPhI}$ or $[(\text{Et}_2\text{O})\text{CaPh}_2]_4 \cdot (\text{Et}_2\text{O})\text{CaO}$ [18] from THF cleavage with diphenylcalcium in diethylether. The H atoms of acetylene are very acidic and therefore, still present naphthylcalcium halide deprotonates $\text{HC}\equiv\text{CH}$ immediately yielding acetylide $(\text{C}_2)^{2-}$. Due to the fact that free acetylene was not observed, it could also be the case that the carbenoid is deprotonated again before CaX_2 and CaO were liberated. The addition of chloro-trimethylsilane yields trimethylsilylnaphthalene from **2** and bis(trimethylsilyl)acetylene from the newly formed acetylide. A similar decomposition reaction was found for **3**, X being the bis(trimethylsilyl)amido group.

3. NMR spectroscopy

The calcium-bound naphthalide anions of **1–3** show a low field shift for the $^{13}\text{C}\{^1\text{H}\}$ NMR resonance of C1 of approximately $\delta = 196$. Such a low field shift is characteristic for calcium-bound aryl groups (Table 1). The coordination number of calcium as well as the second anionic ligand play a negligible role on the chemical shifts of the naphthyl carbon atoms. This observation is in agreement with the assumption that calcium–carbon bonds of organocalcium compounds display mainly an ionic character.

4. Molecular structures

The molecular structure of $[(\text{thf})_4\text{CaBr}_2] \cdot \text{naphthalene}$ (**4**) is shown in Fig. 2. The naphthalene atoms are marked with the letter “N”. The calcium dihalide and naphthalene

Table 1

Comparison of the chemical $^{13}\text{C}\{^1\text{H}\}$ shifts of the calcium-bound carbon atoms of naphthylcalcium halides as well as their selected structural parameters with the phenyl derivatives of the type $(\text{thf})_n\text{Ca}(\text{C}_6\text{H}_2\text{-}2,6\text{-R}_2\text{-}4\text{-R}')\text{X}$

<i>R</i> _{ortho}	<i>R'</i> _{para}	X	$\delta(^{13}\text{C}_{\text{ipso}})$	M–C	M–O	Lit.
H	H	I	190.3	257.4	238	[21]
H	H	Br	190.0	258.3	238.7	[21]
H	Me	I	185.3	255.6	238.2	[21]
Me	Me	I	182.5	257.4	240.6	[22]
Naphthyl		I	195.4	255.2	238.4	[17]
Naphthyl		Br	196.8	252.8	240.5	

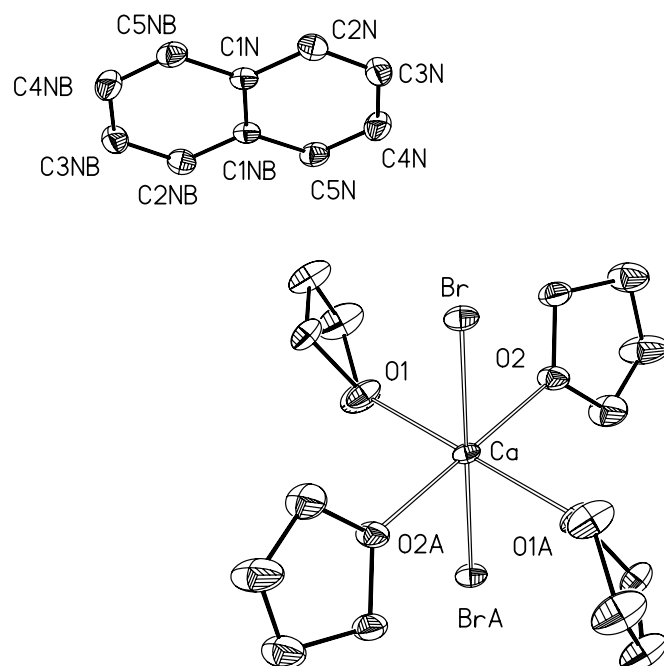


Fig. 2. Molecular structure of $[(\text{thf})_4\text{CaBr}_2] \cdot \text{naphthalene}$ (**4**). The ellipsoids represent a probability of 40%, H atoms are neglected for clarity reasons. The numbering of the naphthalene molecule contains the letter “N”. Symmetry-equivalent atoms are marked with the letters “A” ($-x + 1, -y, -z + 1$) and “B” ($-x, -y + 1, -z + 1$). Selected bond lengths (pm): Ca–Br 284.25(3), Ca–O1 236.8(2), Ca–O2 237.3(2), C1N–C1NB 141.4(7), C1N–C5NB 141.1(5), C1N–C2N 141.0(6), C2N–C3N 136.0(6), C3N–C4N 140.8(6), C4N–C5N 136.0(6).

cocrystallized without short contacts between the alkaline earth metal and the arene. Both molecules exhibit inversion symmetry. Due to the lack of steric strain rather short Ca–O distances (average 237.1 pm) are observed. The Ca–Br bond length shows a value of 284.25(3) pm. The naphthalene molecule shows short C2N–C3N and C4N–C5N bond lengths of 136.0 pm whereas the other C–C distances display an average value of 141, 3 pm. All C–C–C angles of the arene show values close to 120° .

Molecular structure and numbering scheme of centrosymmetric $[(\text{thf})_3\text{Ca}(\text{Naph})\text{Br}]_2$ (**2**) are represented in Fig. 3. The molecular structure consists of two octahedrally coordinated calcium atoms with bridging bromine atoms

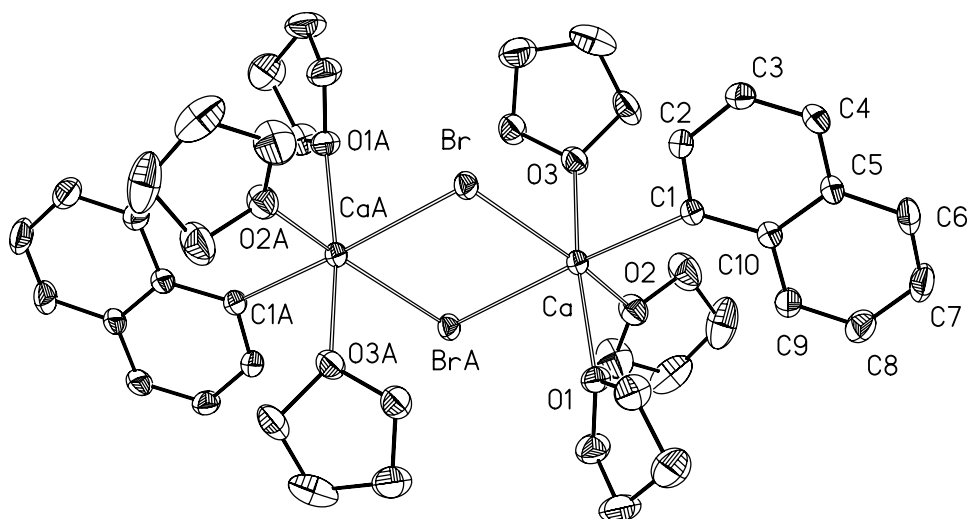


Fig. 3. Molecular structure of $[(\text{thf})_3\text{Ca}(\text{Naph})\text{Br}]_2$ (**2**). The ellipsoids represent a probability of 40%. Hydrogen atoms are omitted for clarity reasons. Symmetry-equivalent atoms are marked with the letter "A" ($-x+2, -y+1, -z$). Selected bond lengths (pm): Ca–C1 252.8(4), Ca–Br 293.41(8), Ca–BrA 294.57(8), Ca–O1 241.0(3), Ca–O2 240.6(3), Ca–O3 239.9(3), C1–C2 138.1(5), C1–C10 143.8(5), C2–C3 141.3(6), C3–C4 136.4(6), C4–C5 141.0(6), C5–C6 141.8(6), C5–C10 142.9(5), C6–C7 135.0(7), C7–C8 141.1(7), C8–C9 137.1(6), C9–C10 141.8(5); angles ($^\circ$): C1–Ca–Br 96.54(9), C1–Ca–BrA 173.6(1), C1–Ca–O1 89.2(1), C1–Ca–O2 98.5(1), C1–Ca–O3 89.8(1).

giving two octahedrons with a common edge. The Ca–Br distances show values of 293.41(8) and 294.57(8) pm and are larger than those of **4**. The planar Ca_2Br_2 ring shows the larger angle at the bromine atom (Ca–Br–CaA $98.60(2)^\circ$) due to the larger repulsion between the doubly positive cations.

The Ca–C bond length of 252.8(4) pm is smaller than those of $(\text{thf})_4\text{Ca}(\text{Naph})\text{I}$ [17] and all other known arylcalcium halides (Table 1). The naphthyl group shows a very narrow C2–C1–C10 angle of $113.8(3)^\circ$. This fact results from the repulsion between the sp^2 lone pair at C1 (which directs to the calcium atom) and the neighbouring C–C bonds. This feature is common in arylcalcium compounds [1,2,21]. Furthermore, the Ca–C–C angles differ drastically by nearly 20° due to steric reasons.

Fig. 4 shows the molecular structure of $(\text{thf})_3\text{Ca}(\text{Naph})\text{N}(\text{SiMe}_3)_2$ (**3**) with a penta-coordinate alkaline earth metal atom. Due to the smaller coordination number, the Ca–C1 bond length of 251.4(6) pm is even smaller than found in **2**. In addition the Ca–C–C bond angles are rather similar with values of $121.6(5)^\circ$ and $125.9(4)^\circ$. Due to the smaller coordination number of the calcium atom the naphthyl group directs into the coordination gap. The C2–C1–C10 angle of the naphthyl group shows a value of $112.4(6)^\circ$ and is even smaller than in **2**.

The Ca–N1 bond length of 235.0(4) pm is rather large for a terminally bound $\text{N}(\text{SiMe}_3)_2$ group [23], however, this value is characteristic for a compound with a penta-coordinate calcium atom [24]. The bis(trimethylsilyl)amido substituent with a planar nitrogen atom displays very short N–Si bond lengths with an average value of 167.7 pm. The N–Si bond lengths decrease with growing ionic character of the metal–nitrogen bond [25]. With increasing negative charge on the planar N atom the backdonation from the

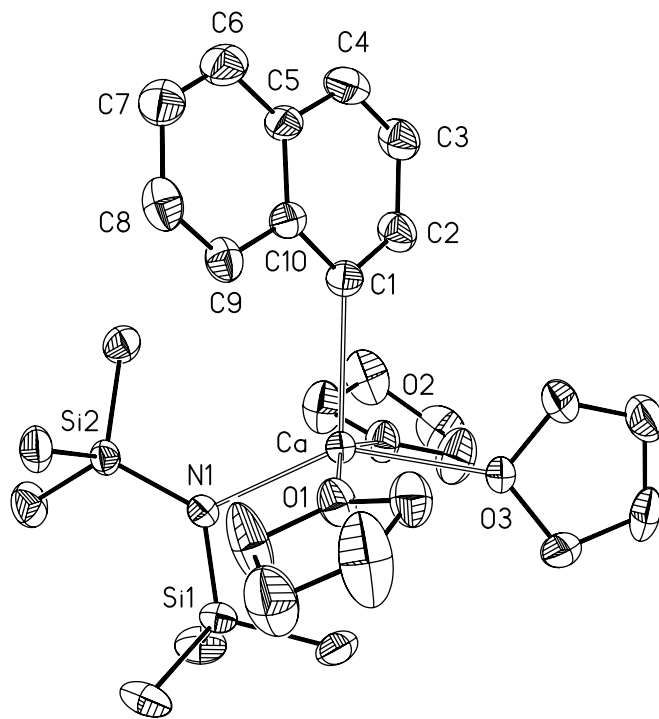


Fig. 4. Molecular structure of $(\text{thf})_3\text{Ca}(\text{Naph})\text{N}(\text{SiMe}_3)_2$ (**3**). The ellipsoids represent a probability of 40%. H atoms are omitted for clarity reasons. Selected bond lengths (pm): Ca–C1 251.4(6), Ca–N1 235.0(4), Ca–O1 238.3(4), Ca–O2 239.5(5), Ca–O3 241.6(4), N1–Si1 166.4(5), N1–Si2 169.0(5), Ca \cdots Si1 328.6(2), Ca \cdots Si2 361.1(2); angles ($^\circ$): C1–Ca–N1 116.5(2), C1–Ca–O1 104.2(2), C1–Ca–O2 91.8(2), C1–Ca–O3 97.9(2), N1–Ca–O1 93.2(2), N1–Ca–O2 92.9(2), N1–Ca–O3 145.3(2), O1–Ca–O2 158.2(2), O1–Ca–O3 82.7(2), O2–Ca–O3 80.4(2), Si1–N1–Si2 125.4(3), Ca–N1–Si1 108.7(2), Ca–N1–Si2 125.9(2).

$\text{p}_z(\text{N})$ lone pair into the $\sigma^*(\text{Si}-\text{C})$ is gaining on importance. Due to the small coordination number of five of the calcium atom, agostic bonds between the Lewis acidic cation

and the trimethylsilyl group distort the trigonal planar coordination sphere of the nitrogen atom. Short Ca··Si1 contacts of 328.6(6) pm lead to a small Ca–N1–Si1 angle of 108.7(2)° whereas the Ca–N1–Si2 value lies at 125.9(2)° leading to a large Ca··Si2 contact of 361.1(2) pm.

5. Conclusion

The THF solutions of the naphthylcalcium derivatives showed no Schlenk equilibrium. These compounds can be recrystallized from THF without the formation of sparingly soluble calcium dihalides. Naphthylcalcium iodide (**1**) in THF is more stable than phenylcalcium iodide whereas **3** is less stable than the THF solution of PhCaN(SiMe₃)₂. The influence of the halide is insignificant; **1** and **2** exhibit comparable stabilities in THF.

The synthesis of these naphthylcalcium derivatives proves the general applicability of the direct synthesis for the preparation of arylcalcium compounds. In order to obtain acceptable yields several preparative conditions have to be realized: (i) Activation of calcium is necessary prior to use because the synthesis has to be applied at low temperatures in order to reduce ether cleavage reactions. (ii) The direct synthesis gives the highest yields in THF solutions, other ethers work less effective. This fact could be due to an effective shielding of the alkaline earth metal cation by the rather strong THF bases. Hydrocarbon solvents represent no suitable solvents. (iii) The aryl iodides give the best results in the direct synthesis of arylcalcium halides whereas the bromides yield arylcalcium derivatives in lower yields. The aryl chlorides and -fluorides show no reactivity towards activated calcium.

Arylcalcium compounds tend to cleave THF at room temperature. This reaction leads to the formation of the corresponding arene and ethane. In course of this ether cleavage also ethenolate can be observed NMR spectroscopically. However, this compound disappeared again because it is deprotonated by still present arylcalcium compound. Derivatization with chloro-trimethylsilane yielded bis(trimethylsilyl)acetylene which suggests the formation of an acetylide from ethenolate. This degradation reaction of the ethenolate also explains the formation of formerly observed oxygen-centered calcium cages such as [((thf)₂Ca-PhI)₃·(thf)CaO] [20] and [((Et₂O)CaPh₂)₄·(Et₂O)CaO] [18]. At low temperatures the degradation of arylcalcium derivatives proceeds very slowly, thus allowing to develop a heavy Grignard-type chemistry.

6. Experimental

6.1. General

All manipulations were carried out in an argon atmosphere under anaerobic conditions. Organocalcium compounds are extremely moisture sensitive and lose coordinated THF already at room temperature once iso-

lated. It was not possible to weigh out a definite amount because the weight of the substances changed permanently during handling and weighing. Therefore, the analysis is limited to NMR and X-ray structure determinations; determination of melting points and elemental analysis gave no reproducible results. ¹H NMR and ¹³C NMR spectra were recorded at [D₈]THF solutions at ambient temperature on a Bruker AC 400 MHz spectrometer. All spectra were referenced to deuterated THF as an internal standard. The assignment of the resonances was confirmed by 2-dimensional NMR-spectroscopy (¹H, ¹H-COSY, HSQC, HMBC). Prior to use, THF was thoroughly dried and distilled in an argon atmosphere. Calcium (99%) and 1-bromonaphthalene (97%) were purchased from Alfa Aesar and used without further purification. Calcium was activated prior to use according to a literature procedure [21]. Potassium bis(trimethylsilyl)amide (95%) was purchased from Aldrich. 1-Naphthylcalcium iodide (**1**) was prepared according to a literature procedure [17].

6.2. Synthesis of bis[tris(tetrahydrofuran)-1-naphthylcalcium bromide] (**2**)

Activated calcium (1.27 g, 31.7 mmol) was suspended in 50 mL of THF and 1-bromonaphthalene (3.28 g, 15.8 mmol, 0.5 equiv.) was added dropwise at ambient temperature. The resulting suspension was shaken for 7 h. Thereafter, unreacted calcium was removed by filtration and the conversion of 52% was determined by acidic consumption of an aliquot. The reddish-brown solution was stored at –90 °C overnight. The next day, 2.13 g of precipitated amorphous 1-naphthylcalcium bromide (**2**) (2.30 mmol, 29%) was collected. Recrystallization from THF and cooling of this solution to 5 °C led to the formation of single crystals of **2**, suitable for X-ray crystallographic studies.

Physical data: ¹H NMR (25 °C, [D₈]THF): δ 1.73 (thf), 3.57 (thf), 6.99 (t, 2H, ³J_{H,H} = 6.4 Hz, H3), 7.06 (quint, 2H, ³J_{H,H} = 6.8 Hz, H7), 7.10 (quint, 2H, ³J_{H,H} = 6.4 Hz, H6), 7.22 (d, 2H, ³J_{H,H} = 7.6 Hz, H4), 7.48 (d, 2H, ³J_{H,H} = 8.0 Hz, H5), 7.87 (d, 2H, ³J_{H,H} = 6.0 Hz, H2), 7.95 (d, 2H, ³J_{H,H} = 7.6 Hz, H8). ¹³C NMR (25 °C, [D₈]THF): δ 25.4 (thf), 67.3 (thf), 122.0 (C6), 122.7 (C4), 123.0 (C7), 124.4 (C3), 128.7 (C5), 134.0 (C10), 137.3 (C8), 138.3 (C2), 146.5 (C9), 196.8 (C1).

6.3. Synthesis of tris(tetrahydrofuran)-1-naphthylcalcium bis(trimethylsilyl)amide (**3**)

To a cooled solution of 1-naphthylcalcium iodide in THF (0.108 M, 40 mL, 4.32 mmol) a solution of KN(SiMe₃)₂ in THF (0.37 M, 11.68 mL, 4.32 mmol) was added dropwise. A colourless precipitate of KI formed immediately. After stirring for an additional hour at 0 °C all solids were removed and the volume of the filtrate was reduced to one quarter of its original volume. Cooling this solution to –90 °C gives crystalline **3** (1.87 g, 3.44 mmol, 80%).

Table 2
Crystal data and refinement details for the X-ray structure determinations of the compounds **2**, **3**, and **4**

Compound	2	3	4
Formula	C ₄₄ H ₆₂ Br ₂ Ca ₂ O ₆	C ₂₈ H ₄₇ CaNO ₃ Si ₂	C ₁₆ H ₃₂ Br ₂ CaO ₄ · C ₁₀ H ₈
Formula weight (g mol ⁻¹)	926.92	541.93	616.48
<i>T</i> (°C)	−90(2)	−90(2)	−90(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.2719(4)	18.333(2)	8.1801(4)
<i>b</i> (Å)	19.5669(7)	8.9517(10)	13.9101(8)
<i>c</i> (Å)	12.4958(5)	20.4965(17)	12.6650(7)
β (°)	97.873(2)	112.249(7)	98.862(3)
<i>V</i> (Å ³)	2245.65(15)	3113.2(6)	1423.90(13)
<i>Z</i>	2	4	2
ρ (g cm ⁻³)	1.371	1.156	1.438
μ (cm ⁻¹)	20.77	3.06	30.54
Measured data	14,942	11,523	11,931
Data with <i>I</i> > 2σ(<i>I</i>)	3339	2944	1872
Unique data/ <i>R</i> _{int}	5127/0.0820	5997/0.1004	3268/0.0759
<i>wR</i> ₂ (all data, on <i>F</i> ²) ^a	0.1301	0.2455	0.1286
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0520	0.0860	0.0462
<i>s</i> ^b	1.019	1.019	1.004
Residual density (e Å ⁻³)	0.838/−0.566	0.442/−0.330	0.687/−0.464
Absorption method	Multi-scan	Multi-scan	Multi-scan
Absorption correction <i>T</i> min/max	0.6545/0.8528	0.7745/0.9528	0.5864/0.6906

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

^b $s = \{ \sum [w(F_o^2 - F_c^2)^2] / (N_o - N_p) \}^{1/2}$.

Physical data: ¹H NMR (25 °C, [D₈]THF): δ 0.02 (s, 18H, Me₃Si), 1.78 (thf), 3.63 (thf), 7.05 (t, 1H, ³J_{H,H} = 8.0 Hz, H3), 7.13 (quint, 1H, ³J_{H,H} = 6.4 Hz, H7), 7.17 (quint, 1H, ³J_{H,H} = 6.4 Hz, H6), 7.29 (d, 1H, ³J_{H,H} = 7.6 Hz, H4), 7.54 (d, 1H, ³J_{H,H} = 7.6 Hz, H5), 7.83 (d, 1H, ³J_{H,H} = 5.2 Hz, H2), 7.88 (d, 1H, ³J_{H,H} = 8.0 Hz, H8). ¹³C NMR (25 °C, [D₈]THF): δ 6.6 (Me₃Si), 25.4 (thf), 67.6 (thf), 122.2 (C6), 123.1 (C4), 123.2 (C7), 124.6 (C3), 128.8 (C5), 134.1 (C10), 137.2 (C8), 137.6 (C2), 145.9 (C9), 195.1 (C1).

6.4. Synthesis of tetrakis(tetrahydrofuran)calcium dibromide · naphthalene (**4**)

After removal of crystalline **2**, the mother liqueur was stored at −90 °C for two weeks. The slow formation of a few colorless crystals of **4** suitable for X-ray structure analysis was observed. NMR investigations showed the values of naphthalene and (thf)₄CaBr₂.

X-ray structure determination of **2**, **3**, and **4** (see Section 7): intensity data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz polarization and for absorption effects [26–28]. Crystallographic data as well as structure solution and refinement details are summarized in Table 2.

The structures were solved by direct methods (SHELXS [29]) and refined by full-matrix least squares techniques against *F*_o² (SHELXL-97 [30]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically

[30]. XP (SIEMENS Analytical X-ray Instruments, Inc.) and POVRAY were used for structure representations.

7. Supplementary material

CCDC 660010, 660011 and 660012 contain the supplementary crystallographic data for **2**, **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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