Organometallic Chemistry

Halide-Free Diarylcalcium Complexes—Syntheses, Structures, and Stability

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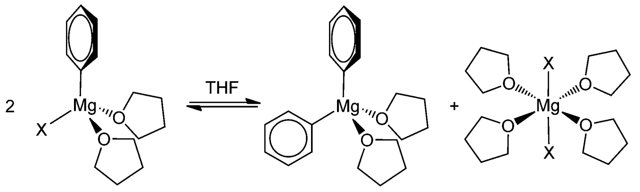
Abstract: A general procedure was developed for the synthesis of diarylcalcium complexes by addition of KO*t*Bu to arylcalcium iodides in THF. Intermediate arylcalcium *tert*-butanolate dismutates immediately leading to insoluble *tert*-butanolate precipitates of calcium. Depending on the steric demand and denticity of additional neutral aliphatic azabases, mononuclear or dinuclear complexes *trans*-[Ca(α-Naph)$_2$(thf)$_4$] (**1**), [Ca(β-Naph)$_2$(thf)$_4$] (**2**), [Ca(Tol)$_2$(tmeda)]$_2$ (**3**), [Ca(Ph)$_2$(tmeda)]$_2$ (**4**), [Ca(Ph)$_2$(pmdta)(thf)] (**5**), [Ca(hmteta)(Ph)$_2$] (**6**), and [Ca([18]C-6)(Ph)$_2$] (**7**) were isolated (Naph = naphthyl; meda = *N,N,N′,N′*-tetramethylethylenediamine; pmdta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine; hmteta = *N,N,N′,N″,N‴,N‴*-hexamethyltriethylenetetramine). The Ca–C bond lengths vary between 250.8 and 263.5 pm, the *ipso*-carbon atoms show low-field-shifted resonances in the ^{13}C NMR spectra.

Introduction

Organolithium and organomagnesium compounds are among the most frequently used organometallic reagents and are indispensable tools in every synthetically working chemist's toolbox,[1,2] whereas the organometallic derivatives of the heavier alkaline earth metals were treated as interesting oddities at best. This is rather surprising given the worldwide accessibility especially of calcium minerals, guarantying the accessibility of this metal at low prices. One of the reasons might be the lack of simple, efficient, and straightforward synthetic strategies for organocalcium halides and diorganocalcium derivatives, in marked contrast to magnesium derivatives for which such strategies are long-known due to the pioneering work of Grignard[3] and Schlenk.[4] In recent years this gap was partially closed by the development of refined synthetic strategies for benzyl,[5] allyl,[6] methanide,[7] and aryl[8] derivatives of calcium and the higher homologues strontium and barium. Especially, the development of a reliable protocol for the efficient synthesis of arylcalcium halides[9,10] in analogy to the well-known synthesis of Grignard reagents raises the hope that the applications of calcium derivatives will one day be as numerous as of their magnesium analogues. However, while a growing number of arylcalcium halides have been isolated and characterized, the diarylcalcium derivatives have stayed singularities[8b] since the protocol developed by Schlenk[4] for the straightforward synthesis of the analogous magnesium derivatives—the precipitation of magnesium dihalides from ether solutions of Grignard reagents by addition of 1,4-dioxane to shift the equilibrium named after him to the right (see Scheme 1)—is not applicable to calcium. In earlier investigations, the transmetalation reaction starting from diarylmercury and calcium shavings was reported to offer a procedure for the preparation of halide-free diarylcalcium.[11] However, the isolation of solvent-free products or products that contained only 0.5 THF ligands per calcium center from such solutions in THF seem unlikely from today's point of view.



Scheme 1. Simplified Schlenk equilibrium to interchange the Grignard reagent PhMgX into MgPh$_2$ and MgX$_2$ (aggregation to oligonuclear complexes not taken into account).

Extending our preliminary study,[12] a straightforward strategy to diarylcalcium complexes is presented in detail and used for a thorough investigation of these elusive derivatives with respect to solid-state structures, solution behavior, and stability.

Results and Discussion

Syntheses and solid-state structures

A more promising route uses arylcalcium halides as starting materials. Like their magnesium counterparts, these calcium-based organometallics exhibit a Schlenk-type equilibrium converting arylcalcium halide into diarylcalcium and calcium dihalide. Already Bogatskii et al.[13] investigated this equilibrium in

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THF in dependency of the reaction conditions and found compositions of [{CaI(Ph)}·{Ca(Ph)$_2$}$_n$] with $0<n<1.2$. Slow fractionated crystallization of a mesitylcalcium iodide solution allowed the isolation of the first structurally characterized complex [Ca(C$_6$H$_2$-2,4,6-Me$_3$)$_2$(thf)$_3$][8b] in low yield. Unfortunately, other derivatives were not accessible by this approach so far. It is well known that the Schlenk equilibrium can be shifted towards diarylmagnesium species of the general formula [(MgR$_2$)$_n$(diox)$_{n+1}$] (diox = 1,4-dioxane) by precipitation of the magnesium dihalides with 1,4-dioxane.[4,14] However, a simple adaptation of this protocol to calcium derivatives was not feasible in our hands. Therefore, another strategy was developed. The metathesis reaction of arylcalcium iodides with potassium *tert*-butanolate in THF is supposed to yield intermediate arylcalcium *tert*-butanolate and insoluble potassium iodide that should precipitate immediately from the reaction solution. Indeed, the presence of major amounts of iodide in the precipitate, obtained from the reaction mixture of [CaI(Ph)(thf)$_4$][10] and potassium *tert*-butanolate, was confirmed by treating a hydrolyzed and acidified sample with AgNO$_3$. The same test gave only an extremely weak positive result for an equally treated sample of the solution. However, additional acidimetric titration (1 M HCl) of the precipitate revealed that the obtained solid also contained about five ninths of the overall alkalinity of the system, whereas four ninths stayed in THF solution. The distribution of benzene and *tert*-butanol among the two fractions of the reaction mixture was further investigated by gas chromatography after hydrolysis. While the precipitate contained predominately *tert*-butanol besides considerable amounts of benzene, in solution almost exclusively benzene was detected after hydrolysis. This finding indicates that intermediate phenylcalcium *tert*-butanolate subsequently formed homoleptic, highly soluble diphenylcalcium and sparingly soluble *tert*-butanolate containing calcium species that precipitated from the reaction mixture. Washing of the residue or use of more diluted solutions did not alter the distribution of alkaline species between precipitate and solution significantly. The insolubility of the precipitate in solvents that are compatible with such highly basic s-block organometallics prevents a more detailed investigation of this solid. The simplified reaction scheme, shown in Scheme 2, summarizes the above-mentioned findings.

Nevertheless, the reaction proved to be highly valuable since it offers a straightforward access to halide-free diarylcalcium derivatives like *trans*-[Ca(α-Naph)$_2$(thf)$_4$] (**1**)[12] and *trans*-[Ca(β-Naph)$_2$(thf)$_4$] (**2**) (Naph = naphthyl). The crystal structure of **2** is shown in Figure 1. These thf adducts form octahedral complexes with *trans*-positioned aryl groups for electrostatic reasons. The observed average Ca–C bond lengths of 262.9 in **1** and 263.5 pm in **2** are similar. The presence of two strongly basic carbanions in the coordination sphere of calcium leads to lengthening of the metal carbon bonds in comparison to naphthylcalcium halide complexes.[9,15–17] For the known compound [Ca(α-Naph){N(SiMe$_3$)$_2$}(thf)$_3$][15] an analogous finding might be expected due to the presence of a strongly basic amide, but here the simultaneous reduction of the coordination number from six to five, which leads to an overall contraction, overcompensates this effect. Selected bond lengths and angles of **1** and **2** are listed together with the corresponding values of naphthylcalcium halides and amides in Table 1.

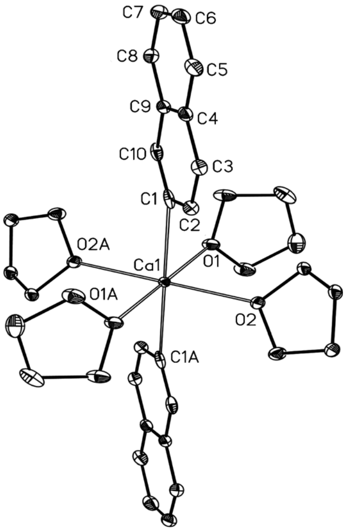
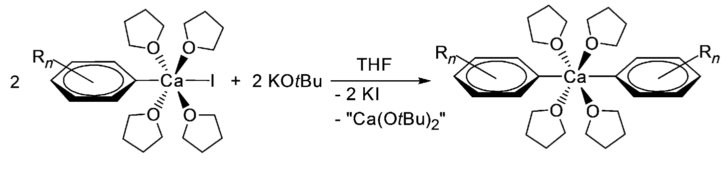


Figure 1. Molecular structure and numbering scheme of **2**. Ellipsoids represent a probability of 40 %, and H atoms are omitted for clarity reasons. Symmetry-related atoms ($-x+1$, $-y$, $-z+1$) are marked with the letter "A". Selected bond lengths [Å]: Ca1–C1 2.635(3), Ca1–O1 2.4047(19), Ca1–O2 2.3790(18). Angles [°]: C1-Ca1-C1A 180.0, C1-Ca1-O1 92.01(7), C1-Ca1-O2 88.80(7), C1-Ca1-O1A 87.99(7), C1-Ca1-O2A 91.20(7), C2-C1-C10 115.9(3).

Table 1. Structural parameters of naphthylcalcium complexes (average values, bond lengths [pm]).

Compound	Ca–C	Ca–X	Ca–O	Ref.
[CaI(α-Naph)(thf)$_4$]	255.2	318.7	234.7	[9]
[CaI(β-Naph)(thf)$_4$]	252.8	319.3	238.5	[17]
[CaI(β-Naph)(thp)$_4$]	253.4	316.6	241.2	[16]
[Ca(μ-Br)(α-Naph)(thf)$_3$]$_2$	252.8	294.0	240.5	[15]
[Ca(Br)(β-Naph)(thp)$_4$]	256.9	299.0	238.0	[17]
[Ca(α-Naph){N(SiMe$_3$)$_2$}(thf)$_3$]	251.4	235.0	239.8	[15]
[Ca(α-Naph)$_2$(thf)$_4$] (**1**)	262.9	–	240.2	[12]
[Ca(β-Naph)$_2$(thf)$_4$] (**2**)	263.5	–	239.2	

Additionally, the above-described protocol was used to prepare solutions of di-*p*-tolylcalcium and diphenylcalcium in THF. The high solubility of these derivatives hinders their isolation in crystalline form, although an amorphous solid of the formal composition [Ca(Ph)$_2$(thf)$_4$][12] was occasionally observed in the latter case. Nevertheless, these solutions are highly useful for the synthesis of a number of donor adducts of diarylcalcium with



Scheme 2. Formation of diarylcalcium.

multidentate nitrogen and oxygen donor ligands. Utilization of such chelating ligands facilitates the isolation of diarylcalcium derivatives and provides an insight into the coordination chemistry of these derivatives in comparison to their arylcalcium halide analogues. The use of *N,N,N′,N′*-tetramethylethylenediamine (tmeda) disclosed that the structural analogies found for phenylcalcium iodides and calcium diiodides cannot be simply extended to the arylcalcium derivatives. While $[CaI(Ph)(tmeda)_2]$[8d] and $[CaI_2(tmeda)_2]$[19] are mononuclear octahedral complexes with a *trans* alignment of the anionic ligands, the use of an excess of bidentate TMEDA leads in the case of the diarylcalcium derivatives to the crystallization of dimers of the type $[(Aryl)Ca(\mu\text{-}Aryl)(tmeda)]_2$ with two terminal and two bridging aryl ligands. The coordination sphere of calcium in $[(Tol)Ca(\mu\text{-}Tol)(tmeda)]_2$ (**3**) (see Figure 2; Tol = 4-methylphenyl), and $[(Ph)Ca(\mu\text{-}Ph)(tmeda)]_2$ (**4**)[12] is remarkable and best described as distorted square pyramidal with the two nitrogen atoms of tmeda and the carbon atoms of the bridging aryl ligands occupying the basal and the terminal aryl ligand the apical position. The two pyramids share a common edge of the basal face with the tips of the pyramids pointing in opposite directions. The calcium atom itself is displaced towards the apical ligand by $\delta = 77$ pm in **3** (61 pm in **4**) from the least-squares plane defined by N1, N2, C8, and C8A (C7 and C7A in **4**).

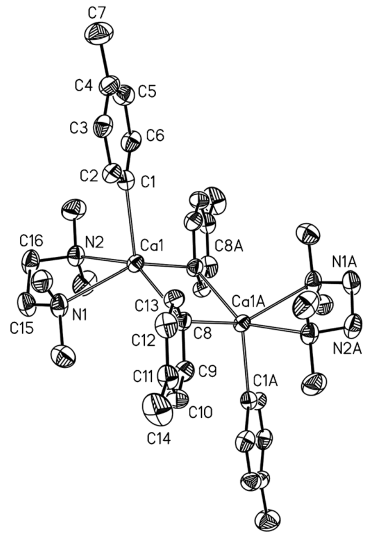


Figure 2. Molecular structure and numbering scheme of **3**. Ellipsoids represent a probability of 40 %, and H atoms are omitted for clarity reasons. Symmetry-related atoms ($-x-1$, $-y$, $-z+2$) are marked with the letter "A". Selected bond lengths [Å]: Ca1–C1 2.600(4), Ca1–C8 2.590(4), Ca1–C8A 2.589(4), Ca1–N1 2.592(3), Ca1–N2 2.570(3). Angles [°]: C1-Ca1-C8 112.02(12), C1-Ca1-C8A 114.69(12), C8-Ca1-C8A 92.49(11), C1-Ca1-N1 101.65(12), C1-Ca1-N2 98.30(11), C8-Ca1-N1 87.92(10), C8-Ca1-N2 146.14(11), C8A-Ca1-N1 140.36(12), C8A-Ca1-N2 88.01(11), C2-C1-C6 116.0(4), C9-C8-C13 112.4(3).

Furthermore it was noticed that the terminal and bridging Ca–C bond lengths of $[(Tol)Ca(\mu\text{-}Tol)(tmeda)]_2$ exhibit very similar values of 259.0(4) and 260.0(4) pm, respectively, whereas for sterically comparable $[(Ph)Ca(\mu\text{-}Ph)(tmeda)]_2$ (**4**) the terminal Ca–C_t distances of 250.8(3) pm are significantly shortened. Since both aryl groups induce comparable intramolecular strain, intermolecular forces and packing effects might be responsible for these unexpected findings. Enhancement of the denticity of the utilized Lewis azabase leads to mononuclear complexes with significantly bent C-Ca-C fragments. Hexa-coordination of the calcium atoms is achieved by an additional THF ligand for the *N,N,N′,N′′,N′′*-pentamethyldiethylenetriamine (pmdta)-stabilized complex *cis*-$[Ca(Ph)_2(pmdta)(thf)]$ (**5**) (Figure 3), whereas the tetradentate *N,N,N′,N′′,N′′′,N′′′*-hexamethyltriethylenetetramine ligand (hmteta) itself shields the calcium atom in *cis*-$[Ca(hmteta)(Ph)_2]$ (**6**) effectively (Figure 4). The observed *cis*-alignment of the phenyl groups is unique for mononuclear octahedral arylcalcium complexes. Here, electrostatic repulsion between the anions only leads to a widening of the angle C-Ca-C to 111.09(10)° in **5** and 109.67(11)° in **6**,

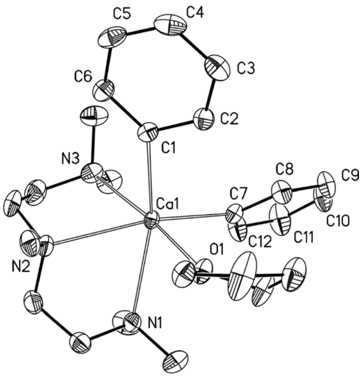


Figure 3. Molecular structure and numbering scheme of **5**. Ellipsoids represent a probability of 40 %. H atoms and a disorder of C15 and C16 are omitted for clarity reasons. Selected bond lengths [Å]: Ca1–C1 2.594(3), Ca1–C7 2.581(3), Ca1–O1 2.465(2), Ca1–N1 2.626(3), Ca1–N2 2.616(3), Ca1–N3 2.655(3). Angles [°]: C1-Ca1-C7 111.09(10), C1-Ca1-O1 83.99(9), C7-Ca1-O1 95.40(9), C1-Ca1-N1 151.05(9), C1-Ca1-N2 92.75(9), C1-Ca1-N3 94.66(10), C7-Ca1-N1 93.79(10), C7-Ca1-N2 151.56(10), C7-Ca1-N3 91.57(10), O1-Ca1-N1 78.98(9), O1-Ca1-N2 102.56(9), O1-Ca1-N3 172.93(9), C2-C1-C6 112.6(3), C8-C7-C12 113.0(3).

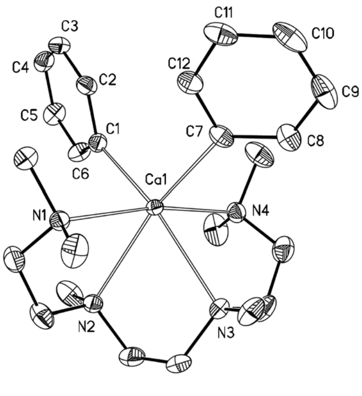


Figure 4. Molecular structure and numbering scheme of **6**. Ellipsoids represent a probability of 40 %, and H atoms are omitted for clarity reasons. Selected bond lengths [Å]: Ca1–C1 2.564(3), Ca1–C7 2.607(3), Ca1–N1 2.631(3), Ca1–N2 2.636(3), Ca1–N3 2.644(3), Ca1–N4 2.579(3). Angles [°]: C1-Ca1-C7 109.67(11), C1-Ca1-N1 94.69(9), C1-Ca1-N2 94.34(10), C1-Ca1-N3 148.53(10), C1-Ca1-N4 89.67(10), C7-Ca1-N1 92.58(9), C7-Ca1-N2 151.68(10), C7-Ca1-N3 95.77(10), C7-Ca1-N4 93.12(10), C2-C1-C6 112.1(3), C8-C7-C12 111.2(3).

but not to the formation of the *trans*-isomer. Obviously, the employed chelating ligands pmdta and hmteta enforce the formation of the *cis*-form in these derivatives. This tendency of tetradentate hmteta to stabilize mononuclear octahedral calcium complexes with a *cis*-alignment was observed earlier for [CaI$_2$(hmteta)][19] and [Ca(hmteta)(PPh$_2$)$_2$].[20] However, in the case of calcium phosphanides it was shown that the difference in energy between the isomers is rather small since [Ca(PPh$_2$)$_2$(thf)$_4$] can be isolated in both forms depending on the crystallization conditions.[20,21] A small difference in energy of 1.97 kcal mol^{-1} was also calculated (DFT) between the *cis* and *trans* form of [Ca(Bz)$_2$(thf)$_4$].[5b] For the arylcalcium derivatives, a similar assumption is reasonable with respect to the results discussed above. Additionally, the dinuclear arylcalcium derivative [Ca(μ-Br)(Phenanthryl)(thf)$_3$]$_2$ was reported recently, in which the terminal phenanthryl ligand occupies a *cis*-position relative to both bridging bromide ions resulting in a facial alignment of the three anionic ligands.[22]

A mononuclear derivative of diphenylcalcium with an unusually large coordination number of eight is realized for the [18]crown-6 adduct (Figure 5). Despite this large coordination number of the alkaline earth metal center a rather short average Ca–C bond of 253.4 pm is observed in [Ca([18]C-6)(Ph)$_2$] (**7**) as the result of the greatly reduced steric pressure of the crown ether relative to four thf ligands. A similar observation was made in the case of [Ca([18]C-6)I$_2$].[19] The Ca–O distances in **7** are large, which indicates that the coordination gap of this crown ether is slightly too large for a calcium cation. Like the related phenylcalcium iodide and calcium diiodide complexes with this ligand,[19] **7** is insoluble in common organic solvents, such as THF, toluene, benzene, and diethyl ether. Attempts to apply other chelating oxygen donor ligands, such as dimethoxyethane, failed probably due to the rapid degradation of arylcalcium compounds in the presence of this ligand.[8e]

Table 2 summarizes selected bond lengths and angles of the investigated complexes **1**–**7**.

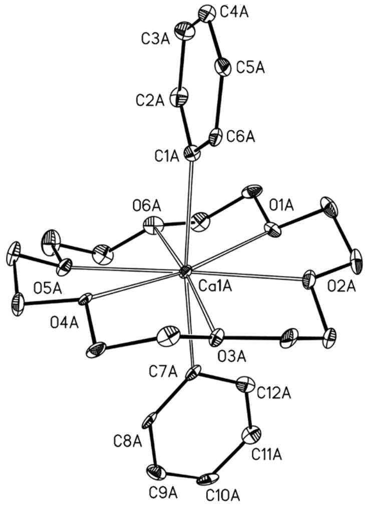


Figure 5. Molecular structure and numbering scheme of **7**. Ellipsoids represent a probability of 40 %, and H atoms are omitted for clarity reasons. Only molecule A of two crystallographically independent molecules is displayed. Selected bond lengths [Å]: Ca1A–C1A 2.536(7), Ca1A–C7A 2.514(7), Ca1A–O1A 2.694(5), Ca1A–O2A 2.600(5), Ca1A–O3A 2.672(5), Ca1A–O4A 2.711(5), Ca1A–O5A 2.662(5), Ca1A–O6A 2.758(5). Angles [°]: C1A-Ca1A-C7A 167.5(2), C1A-Ca1A-O1A 81.9(2), C1A-Ca1A-O2A 84.94(19), C1A-Ca1A-O3A 98.2(2), C1A-Ca1A-O4A 89.86(19), C1A-Ca1A-O5A 96.46(19), C1A-Ca1A-O6A 88.0(2), C7A-Ca1A-O1A 85.9(2), C7A-Ca1A-O2A 91.59(19), C7A-Ca1A-O3A 90.59(19), C7A-Ca1A-O4A 102.3(2), C7A-Ca1A-O5A 87.18(19), C7A-Ca1A-O6A 83.50(19), C2A-C1A-C6A 112.1(6), C8A-C7A-C12A 112.7(6).

Investigations in solution

The solubility of all synthesized diarylcalcium derivatives, except for **7**, in [D$_8$]THF is rather high allowing an investigation of these compounds in solution. The derivative **1** shows a single set of resonances for the metallated α-naphthyl groups in the ^{1}H and ^{13}C NMR spectra. The signal of the calcium-bound carbon atom was observed at $\delta = 198.9$ ppm in the ^{13}C NMR spectrum, significantly shifted downfield relative to the related carbon atom in naphthalene ($\delta = 128$ ppm) under identical conditions. This shift is slightly more pronounced than in α-naphthylcalcium iodide ($\delta = 195.4$ ppm).[9] The observed data of **1** suggests that solution structure and observed solid-state structure are in good agreement with each other. Simple spectra also predestined **1** for further investigation of its stability in THF by NMR spectroscopic measurement. It was determined that half of the compound decomposes by THF degradation within two days at ambient temperature in a two-to-one mixture of THF and [D$_6$]benzene when using cyclohexane as the internal standard (see Figure 6); much faster than related arylcalcium halide derivatives.[16] Among the decomposition products, naphthalene and ethene were identified, which indicated that α-deprotonation of THF and its subsequent cycloreversion occurred as one of the decomposition pathways.

Already in the case of the β-naphthyl derivative **2** it became obvious that the structures of such THF-ligated diarylcalcium derivatives are less uniform in solution than observed for the

Table 2. Structural parameters of diarylcalcium complexes.

Compound	CN	Ca–C$_t$[a]	Ca–C$_{br}$[a]	Ca–N[a]	Ca–O[a]	C$_t$-Ca-C$_t$[a]	Ref.
[Ca(Ph)$_2$(tmeda)]$_2$ (**4**)	5	250.8	259.5	259.0	–	–	[12]
[Ca(Tol)$_2$(tmeda)]$_2$ (**3**)	5	260.0	259.0	258.1	–	–	
[Ca(Mes)$_2$(thf)$_3$]	5	252.0	–	–	238.9	119.6	[8b]
[Ca(α-Naph)$_2$(thf)$_4$] (**1**)	6	262.9	–	–	240.2	176.8	[12]
[Ca(β-Naph)$_2$(thf)$_4$] (**2**)	6	263.5	–	–	239.2	180.0	
[Ca(Ph)$_2$(pmdta)(thf)] (**5**)	6	258.8	–	263.2	246.5	111.1	
[Ca(hmteta)(Ph)$_2$] (**6**)	6	258.6	–	262.3	–	109.7	
[Ca([18]C-6)(Ph)$_2$] (**7**)	8	253.4	–	–	269.2	171.0	

[a] Average values, bond lengths [pm] and angles [°]; CN coordination number of Ca, C$_t$ terminally bound to the *ipso*-carbon atom, C$_{br}$ *ipso*-carbon atom in a bridging position.

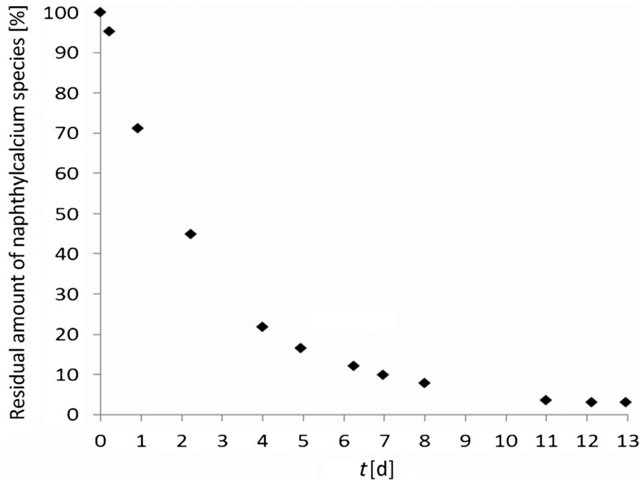


Figure 6. Decomposition of a 0.08 M solution of **1** in THF/[D$_6$]benzene (2:1).

solid state. Despite the use of a pure sample of **2**, a second broad incomplete signal set of a β-naphthyl group became noticeable beside the expected ten signals of this moiety in the ^{13}C NMR spectrum (see the Experimental Section). Additionally the presence of this second species was also observed in the ^{1}H NMR spectrum. Here, two signals for each naphthyl proton in *ortho*-position to the calcium were observed in the region between $\delta = 7.9$ and 8.3 ppm. Nevertheless, the ratio between the sum of the β-naphthyl groups and THF of two to four is in agreement with the solid-state structure.

In the case of diphenylcalcium, solutions in [D$_8$]THF show only very broad signals in both ^{1}H and ^{13}C NMR spectra pointing to a highly fluxional structure of this compound in solution. Similar broad signals were observed in the case of **4** and **5** in [D$_8$]THF besides rather sharp signals of the non-coordinated nitrogen donor ligands tmeda and pmdta, respectively (see Figure 7). This observation clearly shows that the chelating effect of these ligands is not sufficient to suppress their replacement in the coordination sphere of calcium by the excess of deuterated THF used as the solvent.

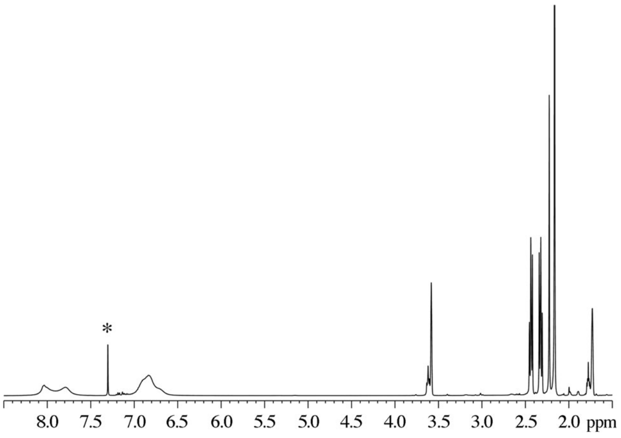


Figure 7. ^{1}H NMR spectrum of **5**.(*=benzene) in [D$_8$]THF.

In case of the hmteta-ligated complex **6**, the opposite observation was made. Here the signals of the calcium bound phenyl groups are well defined in [D$_8$]THF, whereas the signals of the chelating ligand are extremely broad. Although these broad signals indicate fluxionality of the complex and changes in conformation and denticity of the hmteta ligand might be expected, a complete replacement of the ligand by solvent molecules can be excluded. This is somewhat surprising since the NMR spectroscopic data in the case of the related calcium complex [Ca(hmteta)(PPh$_2$)$_2$] in [D$_8$]THF clearly underlines that such an substitution is possible and was achieved for this system.[20] Obviously, the nature of the anion (steric demand, hardness/softness etc) influences the ease of substitution of the neutral ligand in these calcium compounds. Additionally it was noticed during the NMR spectroscopic investigation of **6** that crops of the product that have stayed in contact with the toluene containing mother liquor for extended time spans were contaminated with increasing amounts of benzylcalcium species[5b] as judged by the appearance of typical signals at $\delta = 1.74$, 5.84, 6.51, and 6.56 ppm in the ^{1}H NMR spectrum. This observation underlines the highly basic character of complexes like **6**.

Since the presence of an excess of [D$_8$]THF leads to reversion of the formation of the azabase ligated systems or at least strongly influences their structures in solution, a reinvestigation of these systems with hydrocarbons as solvents was envisioned. While the insolubility of the mononuclear complexes **5** and **6** in benzene and toluene hampered this endeavor, the dinuclear derivatives showed high solubility in these solvents. It was observed that **3** and **4** are fluxional molecules even in [D$_6$]benzene and only one averaged signal set for the interconverting bridging and terminal aryl groups was found in the ^{1}H and ^{13}C NMR spectra of these complexes. Therefore, the chemical shift of the metallated carbon atom of the phenyl group in **4** ($\delta = 186.0$ ppm) expectedly falls between the values found for terminal phenyl groups like in parent [CaI(Ph)(thf)$_4$] ($\delta = 190.3$ ppm)[10] and bridging phenyl groups as observed in [Ca(Cp)(dme)(μ-Ph)]$_2$ ($\delta = 184.5$ ppm; Cp = cyclopentadienide; dme = 1,2-dimethoxyethane).[23]

In general, the ^{13}C NMR spectroscopic data of the investigated complexes show characteristics similar to arylcalcium halides and related aryllithium and arylmagnesium systems. All those derivatives have a strong downfield shift of the metallated carbon atom relative to the parent organic derivative in common, which becomes stronger in the order $\mathrm{Mg} < \mathrm{Ca} \leq \mathrm{Li}$. This downfield shift is slightly more pronounced in terminal than in bridging groups. On this connection, a disagreeing exception should be mentioned. The synthesis of the structurally not characterized diarylcalcium compound [Ca(2-C$_5$H$_3$N-4-CMe$_3$)$_2$(thf)$_2$],[24] containing a metallated pyridine derivative, was described recently. Here, an upfield shift of the calcium bound carbon atom to $\delta = 120.3$ ppm was mentioned. Although this observation might be connected to the introduction of an heteroatom into the aromatic system, it is not only in marked contrast to the results reported above but also to the structurally characterized 2-pyridylmagnesium derivative [Mg$_2$Cl$_2$(μ-2-C$_5$H$_4$N)$_2$(thf)$_3$],[25] which in our hands showed a strong downfield shift of the metallated *ortho* carbon atom of pyridine to $\delta = 210.4$ ppm (*ortho* CH of pyridine: $\delta = 150.6$ ppm) in the ^{13}C NMR spectrum in [D$_8$]THF.

Conclusion

A straightforward strategy towards diarylcalcium derivatives was developed. To observe these products arylcalcium iodides were reacted with potassium *tert*-butanolate in THF under elimination of insoluble KI. Intermediate arylcalcium *tert*-butanolate dismutates immediately and an insoluble precipitate, mainly consisting of calcium bis(*tert*-butanolate) formed and were removed by filtration. Isolation of crystalline THF adducts of diarylcalcium succeeded by cooling of a concentrated THF solution in the case of the naphthyl derivatives [Ca(α-Naph)$_2$(thf)$_4$] (**1**) and [Ca(β-Naph)$_2$(thf)$_4$] (**2**). Although this strategy is also suitable for the phenyl derivative, the addition of multidentate azabases was found to be superior for the isolation of well-defined crystalline products, such as [Ca(Ph)$_2$(tmeda)]$_2$ (**4**), the closely related tolyl derivative [Ca(Tol)$_2$(tmeda)]$_2$ (**3**), [Ca(Ph)$_2$(pmdta)(thf)] (**5**), and [Ca(hmteta)(Ph)$_2$] (**6**). The last two complexes show bent C-Ca-C moieties with bond angles of 111.1 and 109.7°, respectively, and have to be considered the first mononuclear octahedral arylcalcium derivatives with a *cis*-alignment of the anionic ligands. Furthermore, addition of [18]crown-6 ether to solutions of diphenylcalcium in THF gave sparingly soluble [Ca([18]C-6)(Ph)$_2$] (**7**) with an octa-coordinated calcium center.

The application of tmeda as a ligand revealed that diphenylcalcium complexes are not necessarily isostructural to phenylcalcium iodides and calcium diiodides that adopt identical structures in the presence of a variety of neutral donor ligands. As in the case of the related tolyl compound **3**, the use of tmeda yielded a dinuclear phenyl derivative of the formula [Ca(Ph)$_2$(tmeda)]$_2$ (**4**) instead of a mononuclear complex. The coordination sphere of the two calcium atoms in these compounds is best described as square pyramidal with two bridging phenyl groups that connect two neighboring pyramids by a shared edge of the basal face. As a consequence of this unique structure the solubility of these dinuclear complexes in hydrocarbons, such as benzene and toluene, is greatly enhanced. This feature might help to overcome the dependency of the arylcalcium chemistry on solvents like THF and THP which limit the long-term stability of these reagents due to subsequent decomposition reactions.

Experimental Section

General

All manipulations were carried out under an inert argon atmosphere by using standard Schlenk techniques. THF was dried over KOH and distilled over sodium/benzophenone under an argon atmosphere; deuterated THF and benzene was dried over sodium, degassed, and saturated with argon. The yields given are not optimized. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker AC 200, AC 400, or AC 600 spectrometers. Chemical shifts are reported in parts per million relative to Me$_4$Si as an external standard. The residual signals of [D$_8$]THF or [D$_6$]benzene were used as an internal standard.

Calcium was activated by dissolution in liquid NH$_3$ and subsequent reduction of the deep-blue solution to dryness, resulting in finely divided calcium powders. The complexes [CaI(Ph)(thf)$_4$],[10] [CaI(Tol)(thf)$_4$],[10] and [CaI(β-Naph)(thf)$_4$][17] were prepared according to known procedures and recrystallized from THF prior to use. Compounds **1** and **4** were synthesized as preliminarily reported.[12] The calcium content of the products was determined by complexometric titration of a hydrolyzed aliquot with 0.05 M EDTA by using Eriochrome BlackT as an indicator.[26] In the case of complexes containing chelating ligands, prior wet-chemical acid digestion with boiling HNO$_3$ was necessary.

Synthesis of [Ca(β-Naph)$_2$(thf)$_4$] (2)

[CaI(β-Naph)(thf)$_4$] (1.45 g, 2.50 mmol) was dissolved in THF (25 mL) and potassium *tert*-butanolate (281 mg, 2.50 mmol) was added. The resulting suspension was stirred for half an hour at ambient temperature. Thereafter, the formed precipitate was removed by filtration by using a Schlenk frit covered with diatomaceous earth. The volume of the filtrate was reduced to a half by distillation under reduced pressure and the remaining solution was stored at −40 °C for 5 days. The formed yellow crystals were isolated by filtration and were dried in vacuo. The crystals lost non-coordinated THF upon drying. Yield: 213 mg of **1** (0.37 mmol, 29.2 %); ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta = 1.78$ (m, 16 H; CH$_2$ thf), 3.63 (m, 16 H; OCH$_2$ thf), 7.07 (m, 2 H; CH naphthyl), 7.14 (m, 2 H; CH naphthyl), 7.32 (d, 2 H; CH naphthyl), 7.52 (m, 4 H; CH naphthyl), 7.95 + 8.08 (br m, 2 H; CH naphthyl), 8.14 + 8.28 ppm (br m, 2 H; CH naphthyl); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF): $\delta = 25.2$ (8 C; CH$_2$ thf), 67.3 (8 C; OCH$_2$ thf), 122.2 (2 C; CH naphthyl), 122.4 (2 C; CH naphthyl), 123.4 (2 C; CH naphthyl), 127.3 (2 C; CH naphthyl), 127.8 (2 C; CH naphthyl), 132.8 (2 C; quart. C naphthyl), 133.9 (2 C; quart. C naphthyl), 139.4 (2 C; CH naphthyl), 140.7 (2 C; CH naphthyl), 189.0 ppm (2 C; C-Ca); an additional incomplete set of very broad signals was observed: $\delta = 121.9$, 123.2, 139.9, 141.6 ppm; elemental analysis calcd (%) for $C_{36}H_{46}CaO_4$ (582.84 g mol^{-1}): Ca 6.88; found: Ca 7.00. Suitable crystals for X-ray diffraction experiments of the composition [Ca(β-Naph)$_2$(thf)$_4$]·2 THF were obtained by recrystallization in THF and cooling to −40 °C.

Synthesis of [Ca(Tol)$_2$(tmeda)]$_2$ (3)

[CaI(Tol)(thf)$_4$] (2.72 g, 4.98 mmol) was dissolved in THF (40 mL) and solid potassium *tert*-butanolate (559 mg, 4.98 mmol) was added to the stirred colorless solution. The resulting slurry was stirred for half an hour at 0 °C. Thereafter, the formed colorless precipitate was removed by filtration using a Schlenk frit covered with diatomaceous earth and discarded. The orange-colored filtrate was reduced to dryness in vacuo. The resulting orange-colored foam was taken up in tmeda (20 mL) resulting in immediate precipitation (or in some attempts crystallization) of a colorless solid. After 1 h at ambient temperature, the reaction mixture was stored at −20 °C overnight. Afterwards, the formed colorless solid was isolated by filtration and dried in vacuum. The mother liquor was discarded. Yield: 447 mg of **2** (0.66 mmol, 53.1 %); ^{1}H NMR ([D$_6$]benzene, 200 MHz): $\delta = 1.47$ (s, 8 H; CH$_2$ tmeda), 1.54 (s, 24 H; CH$_3$ tmeda), 2.39 (s, 12 H; CH$_3$ tolyl), 7.37 (AA' part of an AA'BB' spin system, 8 H; *m*-CH tolyl), 8.53 ppm (BB' part of an AA'BB' spin system, 8 H; *o*-CH tolyl); ^{13}C{^{1}H} NMR ([D$_6$]benzene, 50.3 MHz): $\delta = 21.9$ (4 C; CH$_3$ tolyl), 45.1 (br, 8 C; CH$_3$ tmeda), 56.3 (br, 4 C; CH$_2$ tmeda), 128.3 (8 C; *m*-CH tolyl), 134.0 (s, 4 C; C tolyl), 142.1 (8 C; *o*-CH tolyl), 181.4 ppm (4 C; Ca-C tolyl); elemental analysis calcd (%) for

$C_{40}H_{60}Ca_2N_4$ (677.104 g mol^{-1}): Ca 11.84; found: Ca 12.07. The almost colorless crystals isolated directly from the reaction mixture in one case were suitable for X-ray diffraction experiments.

Synthesis of [Ca(Ph)$_2$(pmdta)(thf)] (5)

[CaI(Ph)(thf)$_4$] (1.66 g, 3.11 mmol) was dissolved in THF (12 mL) and potassium *tert*-butanolate (349 mg, 3.11 mmol) was added. The resulting suspension was stirred for half an hour at ambient temperature. Thereafter, the formed precipitate was removed by filtration using a Schlenk frit covered with diatomaceous earth. Toluene (5 mL) and pmdta (3.5 mL, 16.76 mmol) were added to the filtrate. Thereafter, THF was removed by distillation under reduced pressure and the remaining solution was stored at −40 °C for one week. The formed pale-orange crystals of the composition [Ca(Ph)$_2$(pmdta)(thf)] were suitable for X-ray diffraction experiments. The crystals were isolated by filtration and were dried in vacuo. Yield: 160 mg of **3** (0.36 mmol, 23.4 %); ^{1}H NMR ([D$_8$]THF, 400 MHz): δ = 1.81 (m, 4H; CH$_2$ thf), 2.20 (s, 12H; CH$_3$ pmdta), 2.26 (s, 3H; CH$_3$ pmdta), 2.35 (m, 4H; CH$_2$ pmdta), 2.47 (m, 4H; CH$_2$ pmdta), 3.65 (m, 4H; OCH$_2$ thf), 6.52–7.26 (brm, 6H; *m*- and *p*-CH phenyl), 7.57–8.50 ppm (brm, 4H; *o*-CH phenyl); ^{13}C{^{1}H} NMR ([D$_8$]THF, 100.6 MHz): δ = 26.4 (s, 2C; CH$_2$, thf), 43.4 (s, 1C; NCH$_3$, pmdta), 46.3 (s, 4C; NCH$_3$, pmdta), 57.3 (s, 2C; NCH$_2$, pmdta), 58.8 (s, 2C; NCH$_2$, pmdta), 121–131 (very broad overlapping signals, 6C; CH phenyl), 141–145 (very broad overlapping signals, 4C; CH phenyl), 189–194 ppm (very broad signals, 2C; Ca-C phenyl); elemental analysis calcd (%) for $C_{25}H_{41}CaN_3O$ (439.70 g mol^{-1}): Ca 9.12; found: Ca 9.03.

Synthesis of [Ca(hmteta)(Ph)$_2$] (6)

[CaI(Ph)(thf)$_4$] (1.76 g, 3.31 mmol) was dissolved in THF (15 mL) and solid potassium *tert*-butanolate (371 mg, 3.31 mmol) was added to the stirred colorless solution. The resulting suspension was stirred for half an hour at 0 °C. Thereafter, the formed colorless precipitate was removed by filtration using a Schlenk frit covered with diatomaceous earth and discarded. Toluene (10 mL) and hmteta (762 mg, 3.31 mmol) were added to the orange-colored filtrate by syringe. To remove most of the THF, the volume of the solution was afterwards reduced to 10 mL by distillation under reduced pressure. Thereafter, the concentrated solution was stored at −40 °C for two days. The formed, almost colorless crystals of the composition [Ca(hmteta)(phenyl)$_2$] were suitable for X-ray diffraction experiments. The crystals were isolated by filtration and were dried in vacuo. Yield: 263 mg of **4** (0.61 mmol, 36.8 %); ^{1}H NMR ([D$_8$]THF, 400 MHz): δ = 1.9–3.2 (brm, 30H; CH$_2$ + CH$_3$ hmteta), 6.72 (m, 2H; *p*-CH phenyl), 6.86 (m, 4H; *m*-CH phenyl), 7.97 ppm (m, 4H; *o*-CH phenyl); ^{13}C{^{1}H} NMR ([D$_8$]THF, 100.6 MHz): δ = 42.5–49.0 (br, 6C; CH$_3$ hmteta), 54.2–59.2 (br, 6C; CH$_2$ hmteta), 122.4 (s, 2C; *p*-CH phenyl), 125.3 (s, 4C; *m*-CH phenyl), 142.0 (s, 4C; *o*-CH phenyl), 191.3 ppm (s, 2C; Ca-C phenyl); elemental analysis calcd (%) for $C_{24}H_{40}CaN_4$ (432.658 g mol^{-1}): Ca 9.14; found: Ca 9.26.

Synthesis of [Ca([18]C-6)(Ph)$_2$] (7)

Potassium *tert*-butanolate (276 mg, 2.46 mmol) was added to a solution of [CaI(Ph)(thf)$_4$] (1.31 g, 2.46 mmol) in THF (7 mL). The resulting suspension was stirred for half an hour at ambient temperature. The formed precipitate was removed by filtration using a Schlenk frit covered with diatomaceous earth. Colorless crystals precipitated during diffusion of a 0.2 M solution of [18]crown-6 in THF in the filtrate at 0 °C. These crystals of the composition [Ca([18]C-6)(phenyl)$_2$] were suitable for X-ray diffraction experiments. The colorless crystals were isolated by filtration and were dried in vacuo. Yield: 195 mg of **5** (0.43 mmol, 35.0 %); elemental analysis calcd (%) for $C_{24}H_{34}CaO_6$ (458.61 g mol^{-1}): Ca 8.74; found: Ca 8.41. Because of the insolubility of the compound in common organic solvents no NMR spectroscopic data could be obtained.

Structure determinations

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo$_{K\alpha}$ radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[27,28] The structures were solved by direct methods (SHELXS[29]) and refined by full-matrix least-squares techniques against Fo^2 (SHELXL-97[29]). The hydrogen atoms of compound **2** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. The crystal of **7** was a non-merohedral twin. The twin law was determined by PLATON[30] to (−0.499, −0.013, −0.5/0.0, −1.0, 0.0/−1.502, 0.038,

Table 3. Crystal data and refinement details for the X-ray structure determinations of the compounds **2**, **3**, and **5**–**7**.

Compound	2	3	5	6	7
Formula	$C_{36}H_{46}CaO_4{\cdot}2\,(C_4H_8O)$	$C_{40}H_{60}Ca_2N_4$	$C_{25}H_{41}CaN_3O$	$C_{24}H_{40}CaN_4$	$C_{24}H_{34}CaO_6$
F_w [g mol^{-1}]	727.02	677.08	439.69	424.68	458.59
T [°C]	−140(2)	−90(2)	−140(2)	−140(2)	−140(2)
crystal system	Triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	8.6069(2)	8.1649(9)	8.4679(4)	8.7260(3)	10.5018(13)
b [Å]	9.3903(2)	19.301(3)	11.6465(6)	11.0921(3)	13.4564(14)
c [Å]	12.8338(4)	12.8576(15)	26.0532(11)	25.8776(8)	19.074(3)
α [°]	75.886(1)	90	90	90	102.566(5)
β [°]	79.536(1)	93.173(8)	98.79(3)	98.223(1)	93.812(6)
γ [°]	86.601(2)	90	90	90	111.010(5)
V [Å^3]	989.08(4)	2023.1(5)	2539.2(2)	2478.93(13)	2424.9(5)
Z	1	2	4	4	4
ρ [g cm^{-3}]	1.221	1.111	1.150	1.138	1.256
μ [cm^{-1}]	2.05	3.12	2.67	2.69	2.94
measured data	6692	12821	12611	14436	10971
data with $I > 2\sigma(I)$	4245	1943	4566	4864	7506
unique data (R_{int})	4404/0.0174	4560/0.1204	5411/0.0337	5562/0.0314	11024/0.0000
wR_2 (all data, on F^2)[a]	0.1718	0.1721	0.2174	0.2225	0.1675
R_1 ($I > 2\sigma(I)$)[a]	0.0654	0.0703	0.0763	0.0801	0.0560
S[b]	1.154	0.978	1.123	1.037	1.079
Res. dens./e Å^{-3}	1.011/−0.474	0.299/−0.245	0.776/−0.626	1.187/−0.648	0.672/−0.384
CCDC no.	969132	969133	969134	969135	969136

[a] Definition of the R indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \mathrm{Max}(F_o^2)]/3$; [b] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

0.499). The contribution of the main component was refined to 0.482(1). All non-disordered, non-hydrogen atoms were refined anisotropically.[29] Crystallographic data as well as structure solution and refinement details are summarized in Table 3. XP (SIEMENS Analytical X-ray Instruments) was used for structure representations. CCDC-969132 (**2**), 969133 (**3**), 969134 (**5**) 969135 (**6**), and 969136 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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