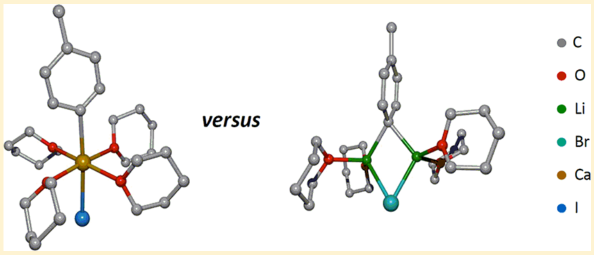
ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

Arylcalcium Iodides in Tetrahydropyran: Solution Stability in Comparison to Aryllithium Reagents

Jens Langer, Mathias Köhler, Reinald Fischer, Feyza Dündar, Helmar Görls, and Matthias Westerhausen*

Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University Jena, Humboldtstrasse 8, D-07743 Jena, Germany

S *Supporting Information*



ABSTRACT: Reduction of para-substituted iodobenzene in tetrahydropyran (THP) with finely dispersed calcium powder yields arylcalcium iodides of the type $[(THP)_4Ca(C_6H_4\text{-}4\text{-}R)I]$ with R = CH_3 (**1**), Cl (**2**), Br (**3**), I (**4**), OCH_3 (**5**). A 2-fold insertion of calcium into dihalobenzenes was not observed. The β-naphthylcalcium iodide $[(THP)_4Ca(\beta\text{-Naph})I]$ (**6**) is also accessible by direct synthesis in THP. The durability of arylcalcium compounds in THP was studied in comparison to that in THF, and a slightly enhanced lifetime in THP at ambient temperature was observed. Furthermore, the relative reactivity and selectivity of **1** and its lithium counterpart $[\{(THP)_2Li\}_2(\mu\text{-Tol})(\mu\text{-Br})]$ (**7**) in the reaction with THP and THF were studied. α-Metalation and subsequent cycloreversion was the major pathway observed for THF in both cases. In the degradation reaction induced by **7**, several byproducts arising from carbolithiation and, surprisingly, from β-metalation reactions were identified, while **1** was found to be more selective. The related $[(THP)_2Li(\mu\text{-Ph})]_2$ (**9**) was prepared and used to unambiguously identify some of the products. In order to verify the formation of benzyllithium as one of the byproducts, an authentic sample of $[(dme)Li(\mu\text{-}CH_2Ph]_2$ (**8**) was prepared. In THP, an inversion of the relative reactivity of **1** and **7** was observed and the calcium compound was found to be more reactive than its lithium analogue. The crystal structures of **1**−**9** were determined by X-ray diffraction studies, and a trans arrangement of the anionic ligands due to electrostatic reasons was observed in case of the hexacoordinated calcium complexes.

■ INTRODUCTION

The year 2005 marked the occurrence of the first structurally characterized arylcalcium derivatives, independently prepared by the groups of Niemeyer,[1] Harder,[2] and Westerhausen,[3] using different synthetic strategies. During the following years arylcalcium derivates emerged from elusive academic curiosities to an easily accessible group of substances.[4]

These compounds show tremendous potential and might be able to challenge the well-established aryllithium derivatives in organic and organometallic syntheses. The worldwide accessibility of calcium, its low price, and its nontoxic behavior regardless of concentration further encourage subsequent investigations. Given its position in the periodic table, the alkaline-earth metal calcium is expected to combine typical properties of s block metals (saltlike behavior, highly heteropolar metal−carbon bonds) and early transition metals (Lewis acidity of cations, d orbital participation, and catalytic activity) within its compounds. Considering a few preconditions, convenient high-yield syntheses of solutions of these post-Grignard reagents have been developed recently.[5] These preconditions are as follows:

(i) Activation of calcium succeeds with ammonia, yielding a finely divided highly reactive metal powder.
(ii) The direct synthesis has to be performed in ethereal solutions, preferably in THF.
(iii) Iodoarenes represent the most suitable substrates; bromoarenes give lower yields, whereas chloro- and fluoroarenes show no reaction with activated calcium.
(iv) Heating during direct synthesis should be avoided in order to limit side reactions such as ether degradation.

THF was found to be essential to obtain well-defined products. A number of THF-ligated derivatives were structurally characterized, and hexacoordinated calcium complexes of the general formula $[(THF)_4Ca(Ar)X]$ with the aryl ligand in a position trans to the halide anion were commonly observed.[5−7] Deviating coordination numbers and/or geometries of the THF complexes were found for sterically crowded aryl substituents[8] or dinuclear complexes.[9,10]

In order to further develop arylcalcium derivatives into successful substitutes of broadly applied aryllithium compounds, it is crucial to identify reactions and conditions under which calcium derivatives show superior reactivity compared to the lithium derivatives. The perfect arylcalcium derivative should fulfill the following criteria:

(i) stable at ambient temperature in the solid state and solution
(ii) reactivity equal to or even higher than that of the lithium counterpart
(iii) enhanced selectivity

Received: June 8, 2012
Published: August 13, 2012

(iv) definite composition and ether content in order to provide an exact stoichiometry for reactions

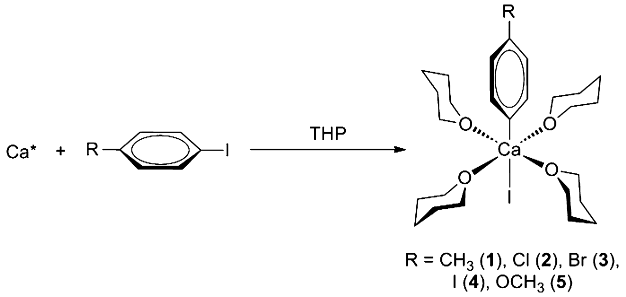
(v) rather high solubility to ensure homogeneous reaction conditions

■ RESULTS AND DISCUSSION

Synthesis. Addressing the shortcomings of the known THF-stabilized arylcalcium halides with respect to solvent degradation, the synthesis and reactivity of post-Grignard reagents in THP were investigated. The smaller ring strain of this solvent molecule compared to that of the commonly used THF should make this cyclic ether less accessible to degradation reactions. However, the higher melting point of THP (mp −49.2 °C) in comparison to that of THF (mp −108.4 °C) limits its use as a solvent at very low temperatures.

In a general synthesis, excess of activated calcium (30 mmol) was suspended in THP and 25 mmol of iodoarene was added at −20 °C (Scheme 1). After several hours of shaking at ambient temperature, excess calcium was removed by filtration and the conversion was determined by acidic titration of an aliquot of the filtrate. A variety of substrates was tested successfully, and conversions comparable to the THF systems were obtained under these conditions.[5,6] The products are readily crystallizing substances, facilitating the isolation of the post-Grignard reagents of the type [$(THP)_4Ca(C_6H_4\text{-}4\text{-}R)I$] (R = CH_3 (**1**), Cl (**2**), Br (**3**), I (**4**), OCH_3 (**5**)) as well as of the *β*-naphthyl derivative [$(THP)_4Ca(C_{10}H_7)I$] (**6**). Acidimetric titration to determine the alkalinity as well as complexometric titration for the calcium content justifies the description of most of the derivatives by the general formula [(THP)$_4$Ca(Aryl)I]. Only the isolated crop of **3** shows overly high alkalinity and calcium content as a result of a lack of selectivity between the C−I and C−Br bonds in the direct synthesis.[11] Nevertheless, the isolated compound contains exclusively the 4-bromophenyl substituent, as judged by NMR experiments. The deviating analytical data are the result of partial substitution of the iodide anion by bromide.

Scheme 1. Synthesis of Post-Grignard Reagents of the Type [(THP)$_4$Ca(Aryl)I]



The crude products obtained were investigated for by-products. [$(THP)_4CaI_2$],[12] formed during the direct synthesis to a minor extent, was found as an impurity of the crude reaction products in some cases, indicated by alkalinity that is slightly too low relative to the calcium content. However, this impurity is present in related THF complexes as well and can be removed easily by recrystallization.

Another type of impurity, commonly observed for the THF systems investigated for comparison, was detected to a minor extent when THP was used, marking the first advantage of this solvent. This impurity was studied in detail by NMR techniques in the case of **1** and identified as a second arylcalcium species.[13] The low-field shift found for the ortho hydrogen atoms of the aromatic ring to δ 8.48 in the ^{1}H NMR spectrum of this species, relative to the signals of **1** (δ 7.62) or its THF counterpart (δ 7.60), is indicative of a bridging tolyl group. This interpretation is further supported by the high-field shift of the ipso carbon atom to δ 180.1 in the ^{13}C NMR spectrum, relative to terminally bound tolyl groups (δ 184.2). A similar trend was also observed for other arylcalcium species containing bridging aryl groups.[14,15] Additionally, an analogous shift was also found for related phenyllithium species containing terminal or bridging phenyl groups, respectively.[16]

This calcium species most likely represents another example of an oxo-centered cluster species, occasionally observed for the aryl derivatives of the heavier alkaline-earth metals.[2,3,17−20] An equilibrium between this compound and **1** can be excluded, since the concentration of this impurity is dependent on the route of the synthesis of **1**. When the THP complexes were prepared from the corresponding THF species, containing this impurity, by ligand exchange, the concentration of this second arylcalcium species was higher than that in crops observed via the direct synthesis route.

Stability and Reactivity. THF degradation by arylcalcium halides was identified earlier as one of the challenges for further applications of these compounds. Thus far, a comprehensive NMR investigation with respect to lifetimes and product spectrum is not available, although some products of the decomposition of arylcalcium iodides in THF were claimed.[8,10,21,22] Therefore, a comparative study of the decomposition of a representative member of the type [$(THP)_4Ca(C_6H_4\text{-}4\text{-}R)I$], namely the *p*-tolyl derivative **1** (Figure 1), was undertaken not only in THP but also in THF to be able to evaluate the stability of arylcalcium species in these solvents under similar conditions. The use of the same batch of starting material ensures the comparability of the runs. On dissolution in THF, the THP ligands of **1** are immediately replaced by THF, which is also present in large excess.

However, these experiments not only serve to establish and compare the relative stabilities of the arylcalcium species in those cyclic ethers but also provide valuable data about the selectivity and reactivity in comparison to those of aryllithium species. Therefore, [$\{(THP)_2Li\}_2(\mu\text{-Tol})(\mu\text{-Br})$] (**7**) (see Figure 2) was included in this study, to allow the first direct comparison of the reactivity of well-defined arylcalcium iodides and aryllithium compounds. The selection of **7** over a homoleptic derivative takes the often dramatic enhancement of the reactivity of organolithium derivatives in the presence of lithium halides into account[23] and makes the lithium compound more comparable to the calcium systems.

When initially studying the reactivity of the THF complexes, generated in situ by addition of an excess of THF to crystalline samples of **1** and **7** in order to obtain reference data for comparison to the THP systems, we found that half of the primary *p*-tolylcalcium derivative was consumed after 8 days at ambient temperature, while the lithium complex was more reactive and half of the starting concentration was already reached after 4 days (see Figure 3). As judged by the formation of ethene, the major pathway of the decomposition reaction in both cases seems to be the *α*-metalation of THF followed by its [3 + 2] cycloreversion, in agreement with earlier studies on the fission of THF by strong bases.[24] The expected products of these processes are in our cases ethene, calcium or lithium ethenolate, toluene, and [$(THF)_4CaI_2$] or LiBr, respectively.

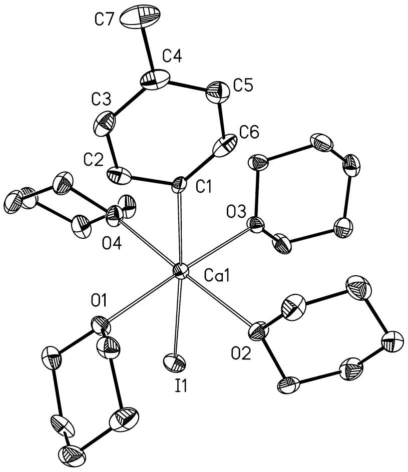


Figure 1. Molecular structure and numbering scheme of [(THP)$_4$Ca(I)C$_6$H$_4$-4-CH$_3$] (**1**). Ellipsoids represent a probability of 40%, and H atoms are omitted for reasons of clarity. The parameters of [(THP)$_4$Ca(I)C$_6$H$_4$-4-OCH$_3$] (**5**) are added in brackets. Selected bond lengths (Å): Ca1−C1 = 2.647(5) [2.643(9)], Ca1−I1 = 3.1571(9) [3.136(2)], Ca1−O1 = 2.384(3) [2.394(5)], Ca1−O2 = 2.402(3) [2.400(6)], Ca1−O3 = 2.438(3) [2.405(5)], Ca1−O4 = 2.383(3) [2.437(5)]. Selected bond angles (deg): C1−Ca1−I1 = 176.4(1) [175.0(2)], C1−Ca1−O1 = 88.2(1) [90.7(2)], C1−Ca1−O2 = 91.5(1) [87.5(2)], C1−Ca1−O3 = 96.6(1) [91.5(2)], C1−Ca1−O4 = 91.8(1) [95.8(2)], O1−Ca1−O2 = 90.1(1) [95.3(2)], O1−Ca1−O3 = 175.2(1) [174.8(2)], O1−Ca1−O4 = 94.0(1) [85.4(2)], O2−Ca1−O3 = 90.4(1) [89.6(2)], O2−Ca1−O4 = 174.8(1) [176.6(2)], O3−Ca1−O4 = 85.3(1) [89.6(2)], I1−Ca1−O1 = 88.77(8) [86.4(1)], I1−Ca1−O2 = 90.39(7) [88.7(1)], I1−Ca1−O3 = 86.41(7) [91.8(1)], I1−Ca1−O4 = 86.49(8) [88.0(1)].

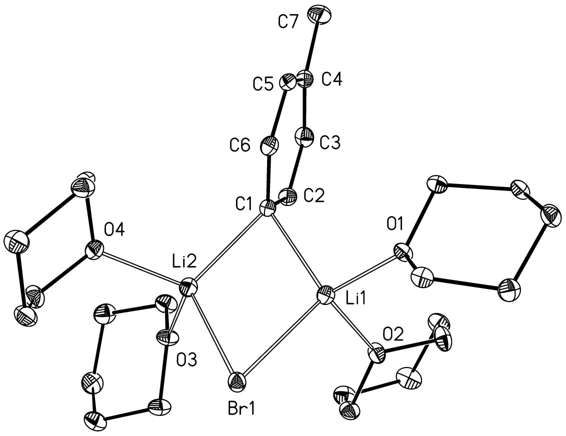


Figure 2. Molecular structure and numbering scheme of [{(THP)$_2$Li}$_2$(μ-Tol)(μ-Br)] (**7**). Ellipsoids represent a probability of 40%, and H atoms are neglected for reasons of clarity. Selected bond lengths (Å): Li1−C1 = 2.207(3), Li2−C1 = 2.210(4), Li1−Br1 = 2.530(3), Li2−Br1 = 2.527(3), Li1−O1 = 1.942(3), Li1−O2 = 1.974(3), Li2−O3 = 2.011(3), Li2−O4 = 1.974(3), Li1···Li2 = 2.677(4). Selected bond angles (deg): Li1−C1−Li2 = 74.6(1), C1−Li1−Br1 = 108.8(1), Li1−Br1−Li2 = 63.9(1), Br1−Li2−C1 = 108.8(1), O1−Li1−O2 = 102.5(1), O3−Li2−O4 = 101.9(2), Li1−C1−C2 = 112.8(1), Li1−C1−C6 = 112.0(1), Li2−C1−C2 = 120.6(2), Li2−C1−C6 = 118.6(2), C2−C1−C6 = 112.2(2).

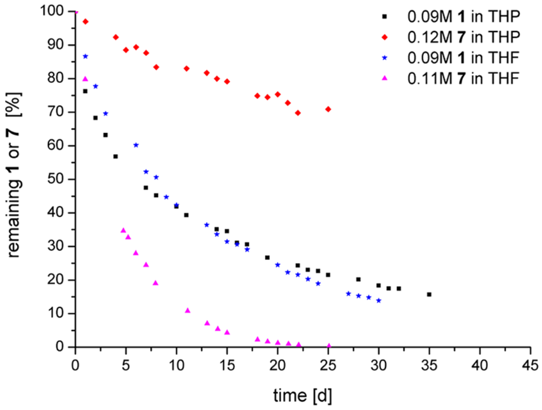


Figure 3. Durability of [(THP)$_4$Ca(I)(p-Tol)] (**1**) and [{(THP)$_2$Li}$_2$(μ-Tol)(μ-Br)] (**7**) in tetrahydrofuran (THF) and tetrahydropyran (THP). The contents of the organometallics were determined by integration of ^{1}H NMR spectra.

While in the case of 7 only one set of signals was observed for the ethenolate species in the ^{1}H and ^{13}C NMR spectra,[25] three distinct sets of signals of calcium ethenolates[26,27] became apparent, although in very low overall concentration (see the Experimental Section and Figure 4).

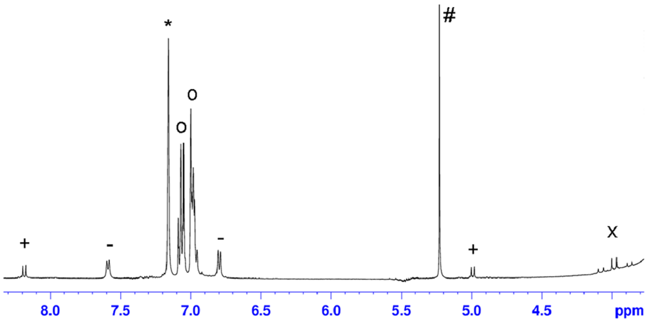


Figure 4. ^{1}H NMR spectrum of the reaction mixture of **1** and THF: (+) unidentified product; (−) residual **1**; (*) residual signal of benzene-d_6; (O) toluene; (#) ethene; (×) calcium ethenolate.

On studying the minor byproducts, in order to gain information about the selectivity of the reactions, we were surprised to find a complete signal set of LiOCH$_2$CH$_2$CH=CH$_2$ in case of the reaction of 7. This product presumably arises from THF, β-attacked by the aryllithium species. Although the fission of THF by organolithium derivatives is a very well studied chemistry[24,28] due to the importance of these compounds, we are not aware of any direct observation of this species, though its presence was rightly concluded from the products observed by quenching experiments or subsequent reactions.[29−31]

Another occurring side reaction is the attack of formed toluene by residual p-tolyllithium species, leading to benzyllithium derivatives. [(dme)Li(CH$_2$C$_6$H$_5$)]$_2$ (**8**) was independently prepared by transmetalation of chlorotribenzylstannane with lithium for comparison reasons to ensure the formation of benzyllithium. The molecular structure of **8** is shown in Figure 5. This complex crystallized as a dimer with a central Li$_2$C$_2$ ring. The tetracoordinate lithium atoms are in significantly distorted tetrahedral environments, with the deviations stemming from a small bite angle of the bidentate bases.

Both lithium compounds present in solution, p-tolyllithium and benzyllithium, additionally insert ethene,[32] formed via the dominating α-elimination reaction of THF, into the lithium−carbon bond, as indicated by the formation of 1-ethyl-4-

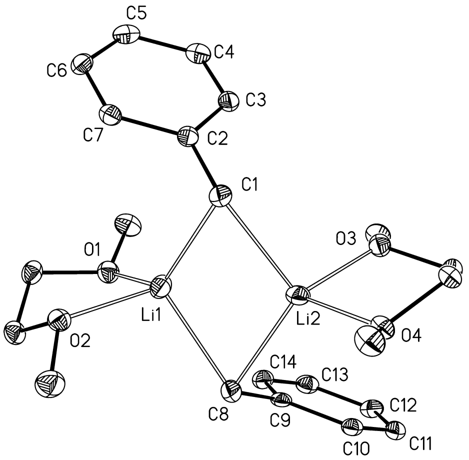


Figure 5. Molecular structure and numbering scheme of $[(\mathrm{dme})\mathrm{Li}(\mu\text{-}\mathrm{CH_2Ph})]_2$ (**8**). The ellipsoids represent a probability of 40%, and H atoms are omitted for reasons of clarity. Selected bond lengths (Å): Li1−C1 = 2.202(7), Li1−C8 = 2.286(6), Li1−O1 = 1.973(6), Li1−O2 = 1.983(6), Li2−C1 = 2.283(6), Li2−C8 = 2.229(7), Li2−O3 = 1.966(6), Li2−O4 = 1.996(6), C1−C2 = 1.454(4), C8−C9 = 1.451(4). Selected bond angles (deg): C1−Li1−C8 = 112.6(2), C1−Li1−O1 = 126.2(3), C1−Li1−O2 = 115.2(3), C8−Li1−O1 = 107.2(3), C8−Li1−O2 = 107.1(3), O1−Li1−O2 = 84.4(2), C1−Li2−C8 = 111.7(2), C1−Li2−O3 = 104.4(3), C1−Li2−O4 = 113.5(3), C8−Li2−O3 = 127.6(3), C8−Li2−O4 = 112.9(3), O3−Li2−O4 = 84.1(2).

methylbenzene as well as *n*-propylbenzene. The identification of those substances is based on the directly observed signals of the ethyl group at δ_H 1.05 (t, CH_3), 2.42 (q, CH_2) and two of the three signals of the *n*-propyl group at δ_H 0.79 (t, CH_3) and 2.42 (t, CH_2) in the ^1H NMR spectrum, while the other signals were only observed by two-dimensional NMR experiments because they overlap with the signals of toluene and THF. In order to ensure their formation, a control experiment was conducted using PhLi as starting material, the THP adduct $[(\mathrm{THP})_2\mathrm{Li}(\mu\text{-}\mathrm{Ph})]_2$ (**9**) of which is shown in Figure 6. This complex crystallized as a dimer with a four-membered Li_2C_2 ring and the alkali metal in distorted-tetrahedral environments. The Li−C bond lengths of 2.20−2.25 Å lie in the expected region for organilithium compounds.

When PhLi was employed in this reaction, the formation of ethylbenzene was expected, containing an ethyl group which should give rise to signals similar to those observed for 1-ethyl-4-methylbenzene, while no formation of benzyllithium is possible and therefore the signals assigned to propylbenzene should not appear. The experiment confirmed these assumptions. Scheme 2 summarizes the occurring reactions in the system **7**/THF.

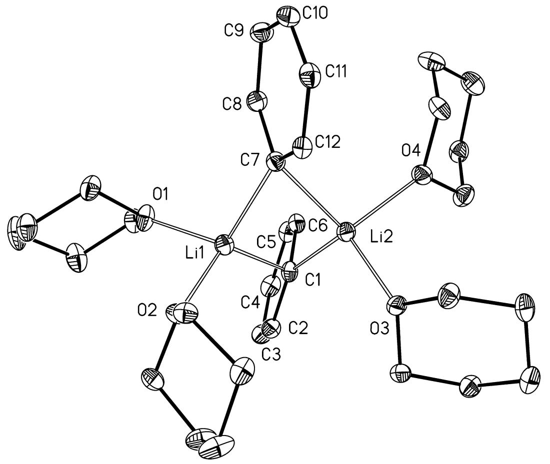
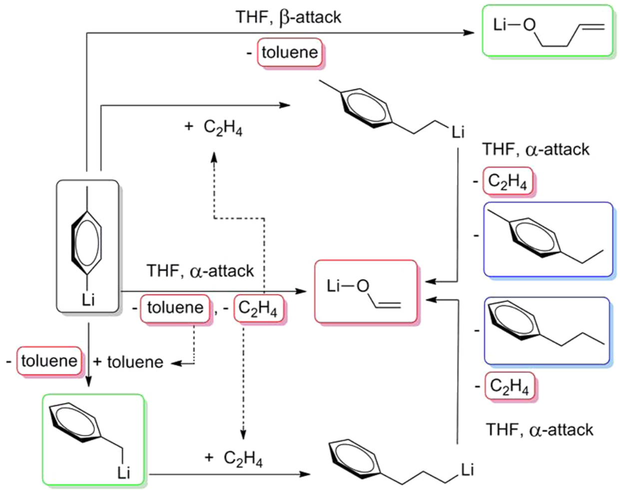


Figure 6. Molecular structure and numbering scheme of $[\{(\mathrm{THP})_2\mathrm{Li}\}(\mu\text{-}\mathrm{Ph})]_2$ (**9**). The ellipsoids represent a probability of 40%, and H atoms are omitted for reasons of clarity. Selected bond lengths (Å): Li1−C1 = 2.227(2), Li1−C7 = 2.213(2), Li2−C1 = 2.197(2), Li2−C7 = 2.245(2), Li1−O1 = 1.981(2), Li1−O2 = 1.983(2), Li2−O3 = 1.966(2), Li2−O4 = 1.979(2), Li1···Li2 = 2.428(3). Selected bond angles (deg): Li1−C1−Li2 = 66.56(8), C1−Li1−C7 = 108.14(9), Li1−C7−Li2 = 65.98(8), C1−Li2−C7 = 108.03(9), O1−Li1−O2 = 97.63(10), O3−Li2−O4 = 99.62(9), Li1−C1−C2 = 111.6(1), Li1−C1−C6 = 114.04(10), Li2−C1−C2 = 141.10(11), Li2−C1−C6 = 101.57(10), C2−C1−C6 = 113.0(1), Li1−C7−C8 = 105.5(1), Li1−C7−C12 = 137.35(10), Li2−C7−C8 = 116.40(10), Li2−C7−C12 = 109.98(9), C8−C7−C12 = 112.9(1).

Scheme 2. Observed Reaction Pathways during Degradation of 7 in THF[a]



[a]Framed substances were observed by NMR measurements: red, major product; blue, minor product; green, trace amounts.

The three side reactions described for the organolithium compound **7** were not observed in case of the calcium derivative **1**. However, here the very low overall concentration of the calcium ethenolate might suggest a subsequent reaction of this species, but further products such as oxo-centered clusters were not detected. Only two additional doublets at δ 8.19 and 4.99 were observed in the ^1H NMR spectrum, related to signals at δ 161.3 and 136.2 in the ^{13}C NMR spectrum. It was confirmed by DEPT and two-dimensional NMR experiments that these signals belong to two CH groups, coupled to each other. The observed shifts make a 1,2-disubstituted alkene derivative more likely than other possibilities,[33,34] but this trace product remained essentially unidentified. Having thoroughly studied the THF systems, we focused our attention on the THP systems. THP as a ligand or solvent is known to be more resistant than THF toward degradation reactions induced by different organolithium compounds. Both protophilic[35] and nucleophilic[36] fission is considerably slowed down: e.g., *n*-BuLi shows a half-life time of 107 ± 3 min in THF but a significantly increased half-life time of 1257 ± 111 min in THP at ambient temperature.[35] The products of THP degradation are unknown, but a ring-opening reaction followed by polymerization was assumed.[35] α-Metalation is likely to be the first step, as suggested by the isolation of complexes containing α-metalated

THP from the reaction mixture of $[(\text{tmeda})\text{Na}(\mu\text{-TMP})(\mu\text{-CH}_2\text{SiMe}_3)\text{Zn}(\text{CH}_2\text{SiMe}_3)]$ and THP.[37]

Against our expectations and also in marked contrast to the observations reported for organolithium derivatives, the use of THP as solvent does not positively affect the durability of the primary calcium species $[(\text{THP})_4\text{Ca}(\text{C}_6\text{H}_4\text{-4-CH}_3)\text{I}]$. Quite the contrary, in early stages of the reaction the decay of this compound is even somewhat more pronounced than in THF (see Figure 3). However, broad overlapping signals in the ranges of δ 8.40−7.90, 6.92−6.78, and 2.08−1.98 in THP point to the formation of secondary *p*-tolylcalcium-containing products, possibly with bridging *p*-tolyl groups. Therefore, the remaining overall content of calcium-bound *p*-tolyl groups is probably higher than that indicated in Figure 3. Assuming that the initial step of the fission of both THF and THP by *p*-tolylcalcium complexes is deprotonation at the α-position (or less likely at the β-position), regardless of the bonding mode of the tolyl substituent or the nuclearity of the compound, the time-dependent formation of toluene would be a good indicator for the overall decrease of *p*-tolylcalcium species. Figure 7 illustrates a slightly slower accumulation of toluene in the reaction mixtures of **1** in THP in comparison to the THF system, which can be interpreted as a slightly stabilizing effect of THP on arylcalcium species relative to THF. Other degradation products, arising from the THP, could not be detected by NMR measurements, but observation of an amorphous precipitate, separating from the reaction mixture in later stages, supports the hypothesis of polymer formation mentioned earlier.[35]

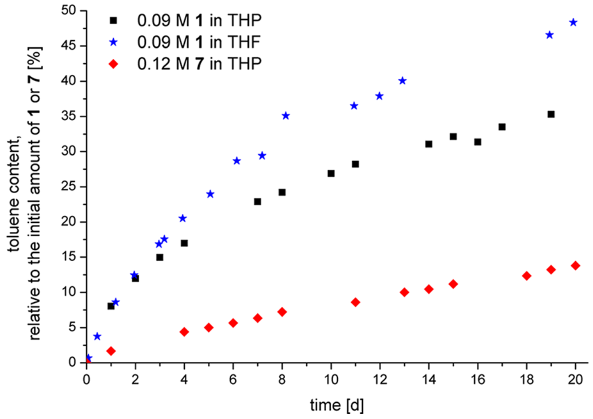


Figure 7. Time-dependent formation of toluene by **1** (and **7**) in THP and THF.[38]

More important than the achieved minor enhancement of the lifespan of *p*-tolylcalcium species in THP is the inversion of the relative reactivity compared to the lithium derivative **7** in this solvent. The calcium compound clearly exceeds the reactivity of its lithium counterpart under similar conditions, as illustrated in Figures 3 and 7.

A reasonable explanation for these differences might be found in the structures of the compounds in solution. While arylcalcium iodides exist predominately as monomers in THF solutions, as judged by the NMR data, and stay this way in THP as well, a much more complex situation is found for aryllithium compounds. In addition to the predominant dimer, containing bridging aryl groups, also substantial amounts of monomers are present in THF.[16,39] Keeping in mind that THP is a less basic[40,41] but slightly more bulky donor ligand, the equilibrium in this solvent should be shifted toward the less reactive dimer. Even the formation of smaller amounts of tetrameric species in equilibrium, as observed in case of diethyl ether as ligand,[42] seems likely. These structural differences between lithium and calcium compounds in solution seem to result in enhanced reactivity of mononuclear *p*-tolylcalcium iodide relative to oligonuclear *p*-tolyllithium in the less polar THP. Furthermore, this advantage in reactivity does not come at the price of lowered selectivity. In contrast, the lithium system was found to be less selective and substantial amounts of benzyllithium were formed by the reaction of *p*-tolyllithium and liberated toluene (see Figure 8).

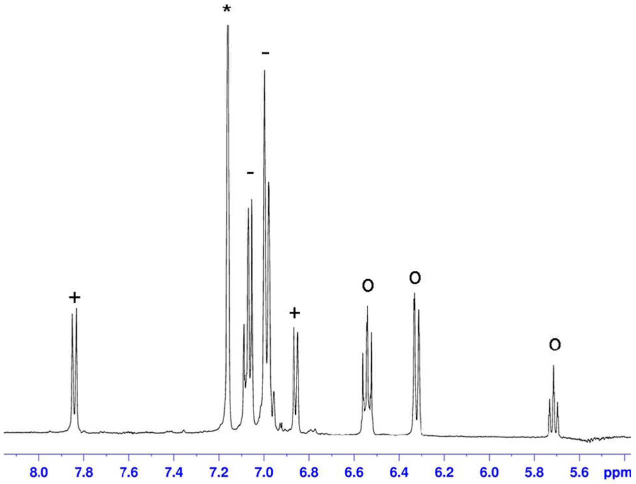


Figure 8. Aromatic region of the ^{1}H NMR spectrum of the reaction mixture of **7** and THP: (+) residual **7**; (*) residual signal of benzene-d_6; (−) toluene; (O) benzyllithium.

In the case of the calcium complex $[(\text{THP})_4\text{Ca}(\text{C}_6\text{H}_4\text{-4-CH}_3)\text{I}]$ no formation of benzylcalcium derivatives, although well-known,[8,43] was detected via NMR measurements under the applied conditions.

These results raise the hope that arylcalcium compounds provide increased reactivity in comparison to aryllithium derivatives, at least in less polar solvents.

Molecular Structures. In order to use arylcalcium compounds as reagents in organometallic chemistry, a well-defined composition of these complexes is desirable to ensure exact stoichiometries in reactions. Crystallization is a powerful tool to achieve this goal, but unfortunately, only a few of the known THF complexes were obtained in the form of well-defined crystals and, hence, the crystal structures for instance of the *p*-halogen-substituted phenyl derivatives are not available. Especially for the most interesting derivative, *p*-iodophenylcalcium iodide, a composition different from that commonly observed was reported for the THF-stabilized complex,[5] indicating an impure product. The use of THP as ligand and solvent was found to be superior and provides a straightforward access to crystals of **1**−**6**, suitable for X-ray diffraction experiments.

The molecular structures of these para-substituted phenylcalcium iodides are rather similar, due to comparable steric demand of the aryl groups in complexes **1**−**6**. As representative examples the structure models of **1**, **2**, **4**, and **6** are displayed in Figures 1 and 9−11, respectively, and selected values of **3** and **5** are added in the figure legends. In addition, bond lengths and

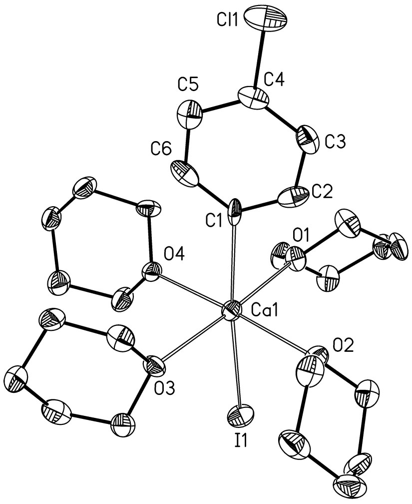


Figure 9. Molecular structure and numbering scheme of [(THP)$_4$Ca(I)C$_6$H$_4$-4-Cl] (**2**). Ellipsoids represent a probability of 40%, and H atoms are neglected for reasons of clarity. Selected bond lengths (Å): Ca1−C1 = 2.643(9), Ca1−I1 = 3.136(2), Ca1−O1 = 2.394(5), Ca1−O2 = 2.400(6), Ca1−O3 = 2.405(5), Ca1−O4 = 2.437(5). Selected bond angles (deg): C1−Ca1−I1 = 175.0(2), C1−Ca1−O1 = 90.7(2), C1−Ca1−O2 = 87.5(2), C1−Ca1−O3 = 91.5(2), C1−Ca1−O4 = 95.8(2), O1−Ca1−O2 = 95.3(2), O1−Ca1−O3 = 174.8(2), O1−Ca1−O4 = 85.4(2), O2−Ca1−O3 = 89.6(2), O2−Ca1−O4 = 176.6(2), O3−Ca1−O4 = 89.6(2), I1−Ca1−O1 = 86.4(1), I1−Ca1−O2 = 88.7(1), I1−Ca1−O3 = 91.8(1), I1−Ca1−O4 = 88.0(1).

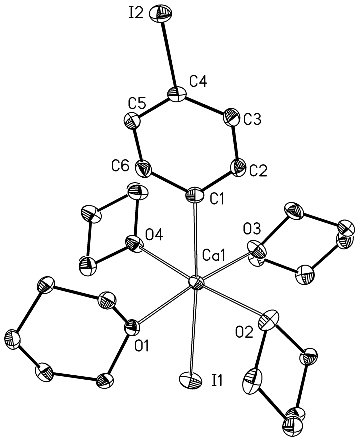


Figure 10. Molecular structure and numbering scheme of [(THP)$_4$Ca(I)C$_6$H$_4$-4-I] (**4**). Ellipsoids represent a probability of 40%, and H atoms are neglected for reasons of clarity. Only molecule A of two crystallographically independent molecules is displayed. The parameters of [(THP)$_4$Ca(I)C$_6$H$_4$-4-Br] (**3**) are added in brackets. Selected bond lengths (Å): Ca1−C1 = 2.565(4) [2.605(9)], Ca1−I1 = 3.1512(8) [3.060(2)], Ca1−O1 = 2.453(3) [2.378(6)], Ca1−O2 = 2.380(3) [2.382(5)], Ca1−O3 = 2.384(3) [2.414(5)], Ca1−O4 = 2.390(3) [2.438(5)]. Selected bond angles (deg): C1−Ca1−I1 = 176.3(1) [174.5(2)], C1−Ca1−O1 = 91.0(1) [90.1(2)], C1−Ca1−O2 = 90.5(1) [85.9(2)], C1−Ca1−O3 = 92.8(1) [92.1(2)], C1−Ca1−O4 = 87.8(1) [94.9(2)], O1−Ca1−O2 = 87.8(1) [98.6(2)], O1−Ca1−O3 = 175.4(1) [172.0(2)], O1−Ca1−O4 = 97.2(1) [83.7(2)], O2−Ca1−O3 = 89.5(1) [89.3(2)], O2−Ca1−O4 = 174.8(1) [177.5(2)], O3−Ca1−O4 = 85.6(1) [88.4(2)], I1−Ca1−O1 = 87.54(7) [87.1(2)], I1−Ca1−O2 = 92.78(7) [89.9(1)], I1−Ca1−O3 = 88.91(8) [91.4(1)], I1−Ca1−O4 = 89.01(8) [89.5(1)].

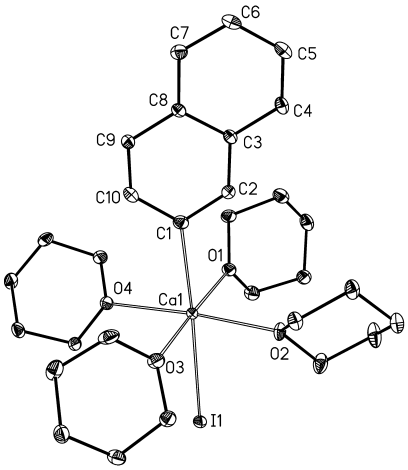


Figure 11. Molecular structure and numbering scheme of [(THP)$_4$Ca(I)(β-Naph)] (**6**). Ellipsoids represent a probability of 40%, and H atoms are neglected for reasons of clarity. Selected bond lengths (Å): Ca1−C1 = 2.534(6), Ca1−I1 = 3.166(1), Ca1−O1 = 2.442(4), Ca1−O2 = 2.386(4), Ca1−O3 = 2.405(4), Ca1−O4 = 2.414(4). Selected bond angles (deg): C1−Ca1−I1 = 176.9(1), C1−Ca1−O1 = 89.7(2), C1−Ca1−O2 = 94.2(2), C1−Ca1−O3 = 89.3(2), C1−Ca1−O4 = 89.0(2), O1−Ca1−O2 = 92.1(1), O1−Ca1−O3 = 176.8(2), O1−Ca1−O4 = 91.0(1), O2−Ca1−O3 = 84.9(1), O2−Ca1−O4 = 175.5(1), O3−Ca1−O4 = 92.0(1), I1−Ca1−O1 = 92.9(1), I1−Ca1−O2 = 87.4(1), I1−Ca1−O3 = 88.3(1), I1−Ca1−O4 = 89.2(1).

angles are given in Table 1. In all of these complexes the anionic ligands are positioned trans, for electrostatic reasons, with only slight deviations from linearity. However, significant distortions result from strongly different proximal and distal Ca−C−C angles, impeding molecular C_2 symmetry. This kind of distortion results from steric strain, because the aryl ring pushes two ether ligands apart and slightly slips between these two coligands. This arrangement enforces significantly different O−Ca−O angles between neighboring THP ligands varying from 83 to 99°. The Ca−C bond lengths of the compounds do not show an obvious trend in relation to the para substituent. However, a long Ca−C bond is always accompanied by a less squeezed C6−C1−C2 angle. There is some indication that elongation of this bond might require only small amounts of energy, due to a rather shallow potential surface. Taking a closer look at the molecular structure of **2**, cigar-shaped thermal ellipsoids were observed for C1, C2, and C6 in the direction of the Ca−C1, C2−C1, and C6−C1 bonds, respectively. This can be interpreted not only as thermal motion but also as an unresolved disorder due to the superposition of at least two slightly different aryl substituents or due to very small amounts of iodine on the aryl positions. A very shallow potential surface with respect to the Ca−C bond length also offers an explanation, and a similar reason was reported for the variation of the Ca−I bond of [(THF)$_4$CaI$_2$], where elongation by 15 pm only requires 1.7 kcal mol^{-1}.[44]

The Ca−I bond length of [(THP)$_4$Ca(C$_6$H$_4$-4-Br)I] (**3**) exhibits an unexpected small value, giving another hint toward partial occupation of this position by bromine. In case of **4**, cocrystallization of small amounts of calcium diiodide was observed, but only one of the two independent molecules within the crystal was affected. Selected structural parameters of the unaffected molecule of **4** together with the other THP adducts of arylcalcium iodides are listed in Table 1.

Tetrahydropyran is the weaker base and more bulky than tetrahydrofuran. Both features support slightly larger Ca−O distances to the THP ligands and averaged values between

Table 1. Selected Structural Parameters (Average Values, Bond Lengths (Å) and Angles (deg), Coordination Number CN of the Metal Atom) of THP Adducts of Aryllithium and Arylcalcium Iodides

	1	2	3	4	5	6	7	9
M	Ca	Ca	Ca	Ca	Ca	Ca	Li	Li
aryl	*p*-Tol	C_6H_4Cl	C_6H_4Br	C_6H_4I	C_6H_4OMe	*β*-Naph	*p*-Tol	Ph
X	I	I	I	I	I	I	Br	
L	THP	THP	THP	THP	THP	THP	THP	THP
CN	6	6	6	6	6	6	4	4
M−C1	2.647	2.643	2.605	2.565	2.550	2.534	2.209	2.221
M−X	3.157	3.136	3.060	3.151	3.156	3.166	2.529	
M−O	2.402	2.409	2.403	2.402	2.416	2.412	1.975	1.977
C1−M−X	176.4	175.0	174.5	176.3	176.3	176.9	108.8	
M−C1−C_{prox}	112.6	115.3	116.5	117.1	123.8	117.1		
M−C1−C_{dist}	129.5	126.4	129.1	130.0	125.6	129.0		
C−C1−C	117.6	118.3	114.3	112.5	112.5	113.8	112.2	113.0

Table 2. Selected Observed and Calculated $^{13}C\{^1H\}$ NMR Data of Arylcalcium Iodides in THP/Benzene-d_6

aryl	$\delta(C_{ipso})$ obsd (calcd)[a]	$\delta(C_{ortho})$ obsd (calcd)[a]	$\delta(C_{meta})$ obsd (calcd)[a]	$\delta(C_{para})$ obsd (calcd)[a]
p-tolyl	183.0 (183.4)	141.2 (140.9)	126.3 (125.8)	130.7 (132.5)
p-Cl-C_6H_4	185.6 (184.5)	142.3 (141.9)	125.1 (125.4)	129.3 (129.6)
p-Br-C_6H_4	186.3 (185.5)	142.9 (143.1)	127.9 (128.5)	118.2 (117.8)
p-I-C_6H_4	186.8 (186.1)	143.3 (143.5)	133.9 (135.1)	90.0 (90.9)
p-MeO-C_6H_4	176.3 (178.4)	141.5 (141.8)	111.7 (110.2)	157.3 (154.5)

[a] $\delta_i = 128.5 + \sum I$; increments *I* for the para substituents were taken from ref 46.

2.402 and 2.416 Å in complexes **1** to **6** were observed. In four related THF complexes, the average Ca−O distances range from 2.38 to 2.406 Å.[5,6,45]

NMR Spectroscopy. In order to establish the influence of the neutral ligand THP on the chemical shift of calcium-bound aryl substituents, a 2/1 mixture of THP and benzene-d_6 was used for ^{13}C NMR measurements, since the commonly used THF-d_8 would immediately replace the THP ligands. These NMR data were compared to those reported for the related THF complexes in THF-d_8 solutions, in which the predominant species probably contains four coordinated THF-d_8 ligands. The most significant differences were obtained for the calcium-bound ipso carbon atoms, which show a characteristic high-field shift of approximately 2 ppm in case of the THP-ligated complexes. When the conditions of the measurements are made even more comparable by using a 2/1 mixture of THF and benzene-d_6, this difference shrinks to little more than 1 ppm. For example, the calcium-bound carbon atom appeared as a singlet in the ^{13}C NMR spectrum of $[(THP)_4Ca(C_6H_4\text{-}4\text{-}CH_3)I]$ (**1**) at δ 185.3 in THF-d_8, δ 184.2 in THF/benzene-d_6, and δ 183.0 in THP/benzene-d_6. These similar data suggest that both the THP- and THF-ligated systems have very similar structures in solution and most likely maintain their solid-state structures.

Prediction of the ^{13}C NMR chemical shifts of the carbon atoms of such calcium-substituted benzenes is possible using well-known empirical increment systems.[46] From the data of **1**−**5**, the empirical increments of the $[(THP)_4CaI]$ substituent can be extracted, being +58.0 (ipso), +12.4 (ortho), −3.3 (meta), and −5.3 ppm (para). Although most increments used in such empirical systems are based upon data obtained in $CDCl_3$, the calculated values show acceptable deviations from the measured values observed for the calcium complexes **1**−**5** (see Table 2). Therefore, the increments reported will help to predict and assign the NMR data of hitherto unknown arylcalcium derivatives.

■ CONCLUSION

Solutions of arylcalcium iodides can be prepared with good yields in tetrahydropyran (THP). The arylcalcium iodides are soluble in this solvent, despite the large electronegativity difference between calcium and carbon and the expected saltlike behavior. This finding should allow application of these post-Grignard solutions in homogeneous calciation, group transfer, and other reactions. The observed arylcalcium iodides are monomeric in THP solution as well as in the solid state, and diverse substituents can be introduced at the para position. The anionic aryl and iodide ligands always are arranged trans to each other for electrostatic reasons. Due to similar steric crowding all of these complexes of the type $[(THP)_4Ca(Aryl)I]$ contain hexacoordinate alkaline-earth-metal centers in distorted-octahedral environments.

The durability of arylcalcium iodide solutions is slightly extended by substitution of the five-membered cyclic ether THF by less strained THP. In comparison to aryllithium compounds, the THP-ligated calcium complexes exhibit an altered reactivity in the deprotonation of THP, proving that calcium complexes indeed are able to outbid well-defined organolithium derivatives under certain reaction conditions. In THF solutions the opposite order of reactivity between lithium and calcium derivatives was observed.

A large benefit of calcium-based organometallics is the metal itself. Calcium is inexpensive, is absolutely nontoxic, is available worldwide, and is easily activated with liquid ammonia, and in addition (in contrast to lithium powder) a nitrogen atmosphere is sufficient for handling of even activated calcium powder. Arylcalcium complexes (post-Grignard reagents) are easily prepared via direct synthesis in THP, are monomeric with hexcoordinate metal centers, have good crystallization properties for purification purposes, have definite compositions of the type $[(THP)_4Ca(Aryl)I]$, have high solubility and reactivity toward substrates, and have a sufficient durability in THP solutions, enabling a rich organometallic chemistry. The only remaining advantage of aryllithium species is their commercial availability, but it is not too temerarious to predict that arylcalcium compounds will also be in trade in the near future.

■ EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under an inert atmosphere (argon or nitrogen) using standard Schlenk techniques. The solvents were dried according to common procedures and distilled under an argon atmosphere; deuterated solvents were 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 MHz, AC 400, and AC 600 spectrometers. Chemical shifts are reported in parts per million. The residual signal of benzene-d_6 (^{1}H NMR, δ 7.16; ^{13}C NMR, δ 128.0) was used as the internal standard. The calcium content was determined by complexometric titration of a hydrolyzed aliquot with 0.05 M EDTA using Eriochrome BlackT as indicator.[47] PhLi and *p*-tolyllithium−lithium bromide were prepared according to known procedures.[48,49] The coordinated diethyl ether was removed under vacuum, and the residue was recrystallized from THP.

Synthesis of [(*p*-tolyl)CaI(THP)$_4$] (1). *Method a.* Activated calcium (1.0 g, 25 mmol) was suspended in tetrahydropyran (40 mL), and 4-iodotoluene (4.36 g, 20 mmol) was added at −20 °C. The resulting suspension was shaken for 6 h without cooling. Thereafter, unreacted calcium was removed by filtration and the conversion (84%) was determined by acidic consumption of an aliquot. The reddish brown solution was stored at −40 °C over 4 days, resulting in a colorless crystalline precipitate of [(*p*-tolyl)CaI(THP)$_4$]. This solid was collected on a cooled Schlenk frit and dried under vacuum. Yield: 4.87 g (8.1 mmol, 40%, crude product).

Method b. Solid [(*p*-tolyl)CaI(THF)$_4$] was dissolved in the minimum amount necessary of THP. The resulting solution was evaporated to dryness under reduced pressure to give [(*p*-tolyl)CaI(THP)$_4$] in essentially quantitative yield.

Anal. Calcd for $C_{27}H_{47}CaIO_4$ (602.65 g mol^{-1}): Ca, 6.65. Found: Ca, 6.62. ^{1}H NMR (THF/benzene-d_6 2/1, 400 MHz): δ 1.34 (m, 16H, CH_2 THP), 1.41 (m, 8H, CH_2 THP), 2.13 (s, 3H, CH_3 tolyl), 3.44 (t, 16H, $^{3}J_{H,H}$ = 5.2 Hz, OCH_2 THP), 6.79 (AA′ part of an AA′BB′ spin system, 2H, *m*-CH tolyl), 7.60 (BB′ part, 2H, *o*-CH tolyl). ^{13}C{^{1}H} NMR (THF/benzene-d_6 2/1, 400 MHz): δ 21.5 (CH_3 tolyl), 23.9 (4 × CH_2 THP), 27.1 (8 × CH_2 THP), 68.6 (8 × CH_2 THP), 126.1 (2 × *m*-CH tolyl), 130.4 (*p*-C tolyl), 141.0 (2 × *o*-CH tolyl), 184.2 (Ca-*i*-C tolyl). An additional signal set of low intensity of a calcium bound tolyl group was observed: ^{1}H NMR (THF/benzene-d_6 2/1, 400 MHz): δ 2.02 (s, 3H, CH_3 tolyl), 6.80 (AA′ part of an AA′BB′ spin system, 2H, *m*-CH tolyl), 8.48 (BB′ part, 2H, *o*-CH tolyl). ^{13}C{^{1}H} NMR (THF/benzene-d_6 2/1, 400 MHz): 21.2 (CH_3 tolyl), 127.0 (2 × *m*-CH tolyl), 133.9 (*p*-C tolyl), 143.9 (2 × *o*-CH tolyl), 180.1 (Ca-*i*-C tolyl).

^{1}H NMR (THP/benzene-d_6 2/1, 400 MHz): δ 1.35 (m, CH_2 THP), 1.42 (m, CH_2 THP), 2.15 (3H, s, CH_3 tolyl), 3.47 (t, $^{3}J_{H,H}$ = 5.2 Hz, OCH_2 THP), 6.83 (2H, AA′ part of an AA′BB′ spin system, *m*-CH tolyl), 7.62 (2H, BB′ part, *o*-CH tolyl). ^{13}C{^{1}H} NMR (THP/benzene -d_6 2/1, 400 MHz): δ 21.5 (CH_3 tolyl), 23.9 (CH_2 THP), 27.0 (CH_2 THP), 68.7 (OCH_2 THP), 126.3 (2 × *m*-CH tolyl), 130.7 (*p*-C tolyl), 141.2 (2 × *o*-CH tolyl), 183.0 (Ca-*i*-C tolyl).

Crystals of [(*p*-tolyl)CaI(THP)$_4$] suitable for X-ray diffraction experiments were obtained by cooling a saturated solution of the complex in tetrahydropyran from ambient temperature to −20 °C.

Synthesis of [(*p*-chlorophenyl)CaI(THP)$_4$] (2). Activated calcium (1.2 g, 29.9 mmol) was suspended in tetrahydropyran (40 mL), and 4-chloro-1-iodobenzene (5.96 g, 25 mmol) was added slowly at −20 °C. The resulting suspension was shaken for 1 h at 0 °C and for an additional 4 h without cooling. Afterward the unreacted calcium was removed by filtration through a Schlenk frit, covered with diatomaceous earth. A conversion of 59.4% was determined by acidimetric consumption of an aliquot. After 2 weeks of storage of the brown solution at −40 °C the colorless precipitate that formed was finally collected on a Schlenk frit and dried in vacuo. Yield: 4.1 g (6.6 mmol, 26.3%). Anal. Calcd for $C_{26}H_{44}CaClIO_4$ (623.07 g mol^{-1}): Ca, 6.43. Found: Ca, 6.52. ^{1}H NMR (THP/benzene-d_6 2/1, 400 MHz): δ 1.33 (m, CH_2 THP), 1.40 (m, CH_2 THP), 3.46 (t, *J* = 5.2 Hz, CH_2 THP), 7.01 (AA′ part of an AA′BB′ spin system, 2H, *m*-CH Ph), 7.63 (BB′ part, 2H, *o*-CH Ph). ^{13}C{^{1}H} NMR (THP/benzene-d_6 2/1, 100.6 MHz): δ 23.9 (CH_2 THP), 27.0 (CH_2 THP), 68.7 (OCH_2 THP), 125.1 (2C, *m*-C), 129.3 (1C, C−Cl), 142.3 (2C, *o*-C), 185.6 (1C, C−Ca).

Crystals of [(*p*-chlorophenyl)CaI((THP)$_4$] suitable for X-ray diffraction experiments were obtained by cooling a saturated solution of the complex in THP from ambient temperature to −20 °C.

Synthesis of [(*p*-bromophenyl)CaI(THP)$_4$] (3). Activated calcium (1.2 g, 29.9 mmol) was suspended in tetrahydropyran (40 mL), and 4-bromo-1-iodobenzene (7.07 g, 25 mmol) was added slowly at −20 °C. The resulting suspension was shaken for 1 h at 0 °C and for an additional 4 h without cooling. Then the formed precipitate was removed by filtration through a Schlenk frit, covered with diatomaceous earth. The residue on the filter was dried in vacuo and suspended in THP (60 mL), and the suspension was stirred for 1 h at ambient temperature. The solution obtained after filtration was combined with the mother liquor. A conversion of 60.7% was determined by acidimetric consumption of an aliquot of the combined solutions. After 1 day of storage of the brown solution at −40 °C the colorless precipitate that formed was collected on a Schlenk frit and dried in vacuo. Yield: 3.05 g (4.6 mmol, 18.3%). Anal. Calcd for $C_{26}H_{44}CaBrIO_4$ (667.52 g mol^{-1}): Ca, 6.00. Found: Ca, 6.58. ^{1}H NMR (THP/benzene-d_6 2/1, 400 MHz): δ 1.33 (m, CH_2 THP), 1.40 (m, CH_2 THP), 3.47 (t, *J* = 5.2 Hz, CH_2 THP), 7.17 (AA′ part of an AA′BB′ spin system, 2H, *m*-CH Ph), 7.61 (BB′ part, 2H, *o*-CH Ph). ^{13}C{^{1}H} NMR (THP/benzene-d_6 2/1, 100.6 MHz): δ 23.9 (CH_2 THP), 27.0 (CH_2 THP), 68.8 (OCH_2 THP), 118.2 (1C, C−Br), 127.9 (2C, *m*-C), 142.9 (2C, *o*-C), 186.3 (1C, C−Ca).

Synthesis of [(*p*-iodophenyl)CaI(THP)$_4$] (4). 1,4-Diiodobenzene (8.25 g, 25 mmol) was slowly added to a suspension of activated calcium (1.2 g, 29.9 mmol) in tetrahydropyran (40 mL) at −20 °C. Afterward the resulting suspension was shaken for 1 h at 0 °C and for an additional 4 h without cooling. Additional tetrahydropyran (20 mL) was added after 4 h of shaking. Then the unreacted calcium was removed by filtration through a Schlenk frit, covered with diatomaceous earth. A conversion of 71.3% was determined by acidimetric consumption of an aliquot of the filtrate. The brown solution was stored for 1 week at −40 °C. The colorless precipitate that formed was collected on a cooled Schlenk frit and dried in vacuo. Yield: 3.5 g (4.9 mmol, 19.6%). Anal. Calcd for $C_{26}H_{44}CaI_2O_4$ (714.52 g mol^{-1}): Ca, 5.61. Found: Ca, 5.51. ^{1}H NMR (THP/benzene-d_6 2/1, 400 MHz): δ 1.34 (m, CH_2 THP), 1.40 (m, CH_2 THP), 3.46 (t, *J* = 5.2 Hz, CH_2 THP), 7.30 (AA′ part of an AA′BB′ spin system, 2H, *m*-CH Ph), 7.43 (BB′ part, 2H, *o*-CH Ph). ^{13}C{^{1}H} NMR (THP/benzene-d_6 2/1, 100.6 MHz): δ 23.9 (CH_2 THP), 27.0 (CH_2 THP), 68.7 (OCH_2 THP), 90.0 (1C, C−I), 133.9 (2C, *m*-C), 143.3 (2C, *o*-C), 186.8 (1C, C−Ca).

Recrystallization of the crude product from THP and heptane in a ratio of 1/1 led to crystals suitable for X-ray diffraction experiments (ambient temperature to −40 °C).

Synthesis of [(*p*-methoxyphenyl)CaI(THP)$_4$] (5). *Method a.* 4-Iodoanisole (4.53 g, 19.3 mmol) was slowly added to a suspension of activated calcium (1.2 g, 29.9 mmol) in tetrahydropyran (35 mL) at −20 °C. Afterward the resulting suspension was shaken for 1 h at 0 °C and for an additional 4 h without cooling. Then the unreacted calcium was removed by filtration through a Schlenk frit, covered with diatomaceous earth. A conversion of 61% was determined by acidimetric consumption of an aliquot of the filtrate. The residue on the filter was extracted with additional THP (20 mL), yielding further 4% of the product, adding up to 65% overall conversion. The washing solution was discarded while the brown mother liquor was stored for 1 week at −40 °C. The colorless precipitate that formed was collected on a cooled Schlenk frit and dried in vacuo. Yield: 1.94 g (3.13 mmol, 16.2%).

Method b. Solid [(*p*-methoxyphenyl)CaI(THF)$_4$] (0.53 g, 0.94 mmol) was dissolved in THP (20 mL). The resulting yellowish solution was stirred for 30 min and afterward slowly reduced to dryness under reduced pressure. The off-white residue was dried in vacuo. Then the solid was suspended in *n*-hexane (20 mL), the suspension was stirred for 20 min, and the solid was finally collected on a Schlenk frit. The off-white solid was washed with *n*-hexane (10 mL) and dried under vacuum. Yield: 0.55 g (0.89 mmol, 94%). Anal. Calcd for $C_{27}H_{47}CaIO_5$ (618.65 g mol^{-1}): Ca, 6.48. Found: Ca, 6.53. ^{1}H NMR (THP/benzene-d_6 2/1, 400 MHz): δ 1.35 (m, CH_2 THP), 1.42 (m, CH_2 THP), 3.46 (t, J = 5.2 Hz, CH_2 THP), 6.65 (AA′ part of an AA′BB′ spin system, 2H, *m*-CH Ph), 7.61 (BB′ part, 2H, *o*-CH Ph). ^{13}C{^{1}H} NMR (THP/benzene-d_6 2/1, 100.6 MHz): δ 23.9 (CH_2 THP), 27.0 (CH_2 THP), 54.1 (1C, O−CH_3), 68.7 (OCH_2 THP), 111.7 (2C, *m*-C), 141.5 (2C, *o*-C), 157.3 (1C, C−O), 176.3 (1C, C−Ca).

In the ^{1}H NMR spectra, very broad signals of a second arylcalcium species were observed. The chemical shift points to a bridging *p*-methoxyphenyl moiety. ^{1}H NMR (THP/benzene-d_6 2/1, 400 MHz): δ ~6.73 (v br), 8.21 (v br).

Crystals of [(*p*-methoxyphenyl)CaI(THP)$_4$] suitable for X-ray diffraction experiments were obtained by cooling a saturated solution of the complex in tetrahydropyran from ambient temperature to −20 °C.

Synthesis of [(*β*-naphthyl)CaI((THP)$_4$] (6). Activated calcium (0.4 g, 10.0 mmol) was suspended in tetrahydropyran (35 mL), and *β*-iodonaphthalene (2.11 g, 8.3 mmol) was added slowly at −20 °C. The suspension was shaken for 1 h at 0 °C and for an additional 4 h without cooling. Then the precipitate that formed was removed by filtration through a Schlenk frit, covered with diatomaceous earth. The residue on the filter was dried in vacuo and suspended in THP (40 mL), and the suspension was stirred for 1 h at ambient temperature. The solution obtained after filtration was combined with the mother liquor. A conversion of 75.6% was determined by acidimetric consumption of an aliquot of the combined solutions. After 1 week of storage of the dark violet solution at −40 °C the pale yellow precipitate that formed was finally collected on a Schlenk frit and dried in vacuo. Yield: 1.3 g (2.0 mmol, 24.5%). Anal. Calcd for $C_{30}H_{47}CaIO_4$ (638.68 g mol^{-1}): Ca, 6.28. Found: Ca, 6.16. ^{1}H NMR (THP/benzene-d_6 2/1, 600 MHz): δ 1.33 (m, CH_2 THP), 1.40 (m, CH_2 THP), 3.46 (t, J = 5.2 Hz, CH_2 THP), 7.11 (t, 1H, H7), 7.20 (t, 1H, H6), 7.47 (d, 1H, H4), 7.59 (d, 1H, H5), 7.63 (d, 1H, H8), 7.95 (d, 1H, H3), 8.17 (s, 1H, H1). ^{13}C{^{1}H} NMR (THP/benzene-d_6 2/1, 100.6 MHz): δ 23.9 (CH_2 THP), 27.0 (CH_2 THP), 68.7 (OCH_2 THP), 122.5 (2C, C4+C7), 123.6 (1C, C6), 127.1 (1C, C8), 127.9 (1C, C5), 132.6 (1C, C9), 133.6 (1C, C10), 139.5 (1C, C1), 140.4 (1C, C3), 186.8 (1C, C−Ca).

Crystals of [(*β*-naphthyl)CaI((THP)$_4$]·THP suitable for X-ray diffraction experiments were obtained by cooling a saturated solution of the complex from ambient temperature to −40 °C.

Synthesis of [(THP)$_4$Li$_2$(*μ*-Br)(*μ*-tolyl)] (7). [(*p*-tolyl)Li·LiBr] (0.5 g, 2.7 mmol) was suspended in *n*-heptane (10 mL). THP (1.5 mL) was slowly added to the stirred suspension to give a clear yellowish solution. Then the reaction mixture was stored at −20 °C for 2 days. The crystals that formed were isolated by decantation and dried undervacuum. Yield: 1.02 g (1.93 mmol, 71.5%). ^{1}H NMR (THP/benzene-d_6 2/1, 400 MHz): δ 1.34 (m, CH_2 THP), 1.41 (m, CH_2 THP), 2.14 (3H, s, CH_3 tolyl), 3.43 (t, $^3J_{H,H}$ = 5.1 Hz, OCH_2 THP), 6.85 (2H, AA′ part of an AA′BB′ spin system, *m*-CH tolyl), 7.87 (2H, BB′ part, *o*-CH tolyl). ^{13}C{^{1}H} NMR (THP/benzene-d_6 2/1, 400 MHz): δ 21.6 (CH_3 tolyl), 24.0 (CH_2 THP), 27.1 (CH_2 THP), 68.6 (OCH_2 THP), 126.0 (2 × *m*-CH tolyl), 131.6 (*p*-C tolyl), 144.5 (2 × *o*-CH tolyl), 179.6 (Li-*i*-C tolyl).

Suitable crystals of **6** for X-ray diffraction experiments were obtained directly from the reaction mixture at −20 °C.

Synthesis of [(dme)Li(*μ*-CH$_2$Ph]$_2$·(toluene) (8). In analogy to a known procedure,[50] a solution of benzyllithium was prepared from 2.35 g (5.5 mmol) of tribenzyltin chloride and 4 equiv of methyllithium in diethyl ether (25 mL). The precipitate of LiCl that formed was removed by filtration, and the mother liquor was reduced to dryness in vacuo. The resulting residue was recrystallized using a mixture of toluene and DME (ambient temperature to −40 °C). The colorless needles that formed were collected on a Schlenk frit, washed with cold toluene (10 mL) and cold diethyl ether (10 mL), and dried under vacuum. Yield: 1.16 g (2.48 mmol; 30%) of [(dme)Li(μ_2-CH_2Ph)]$_2$·$PhCH_3$. ^{1}H NMR (benzene-d_6, 200.1 MHz): δ 1.65 (4H, s, CH_2Ph), 2.11 (3H, s, CH_3), 2.86 (8H, s, O−CH_2), 2.94 (12H, s, O−CH_3), 6.53 (2H, t, J = 7.0 Hz, *p*-CH), 6.90 (4H, d, J = 7.6 Hz, *o*-CH), 7.10 (4H, dd, J = 7.6 Hz, J = 7.0 Hz, *m*-CH). ^{13}C NMR (benzene-d_6, 50.3 MHz): δ 30.4 (^1J(^{13}C−^{1}H) = 121.4 Hz, Li−CH_2), 58.5 (^1J(^{13}C−^{1}H) = 142.6 Hz, O−CH_3), 70.5 (^1J(^{13}C−^{1}H) = 144.0 Hz, O−CH_2), 111.7 (^1J(^{13}C−^{1}H) = 157.1 Hz, *p*-CH), 120.8 (^1J(^{13}C−^{1}H) = 156.4 Hz, CH), 128.2 (^1J(^{13}C−^{1}H) = 163.9 Hz, CH), 159.2 (*i*-CH).

Synthesis of [(THP)$_4$Li$_2$(*μ*-Ph)$_2$] (9). A sample of [(Et_2O)Li(*μ*-Ph)]$_4$, prepared according to a known procedure,[48] was dried under vacuum to remove coordinated diethyl ether. Subsequent recrystallization from a THP/heptane mixture (ratio 1/2) gave crystals of **9**. The crystals were suitable for X-ray diffraction experiments. A yield was not determined. ^{1}H NMR (THF/benzene-d_6 2/1, 400 MHz): δ 1.34 (m, 16H, CH_2 THP), 1.41 (m, 8H, CH_2 THP), 3.44 (t, 16H, $^3J_{H,H}$ = 5.2 Hz, OCH_2 THP), 6.91 (m, 2H, *p*-CH Ph), 7.01 (m, 4H, *m*-CH Ph), 8.02 (m, 4H, *o*-CH, Ph).

Reactivity Studies. A sample of **1** or **7** was dissolved in 0.4 mL of THF or THP in a sealable NMR tube. Benzene-d_6 (0.2 mL) was added, and the tube was sealed with a Teflon screw cap afterward. The sample was immediately measured, stored in a room kept at 22 °C, and remeasured approximately every 24 h. The residual signal of benzene-d_6 was used as an internal standard for both integration and chemical shift. The decay of aryl species was followed by integrating the downfield part of the AA′BB′ spin system of the *p*-tolyl substituent.

Observed Calcium-Containing Species. "XCa(O−CH═CH_2)": three different species A−C (ratio approximately 1/2.5/1) in THF; signals marked with an asterisk overlap with other signals and were observed via HSQC and HMBC experiments.

^{1}H NMR (THF/benzene-d_6 2/1, 400 MHz): A, δ 3.58 (1H, ═CH_2, *), 3.98 (d, $J_{H,H}$ = 13.7 Hz, 1H, ═CH_2), 7.05 (1H, O−CH═, *); B, δ 3.60 (1H, ═CH_2, *), 3.87 (d, $J_{H,H}$ = 13.7 Hz, 1H, ═CH_2), 7.30 (dd, $J_{H,H}$ = 13.8 Hz, $J_{H,H}$ = 5.3 Hz, O−CH═); C, δ 3.73 (d, $J_{H,H}$ = 5.8 Hz, 1H, ═CH_2), 4.08 (d, $J_{H,H}$ = 13.9 Hz, 1H, ═CH_2), 7.18 (1H, O−CH═, *). ^{13}C{^{1}H} NMR (THF/benzene-d_6 2/1, 400 MHz): A, δ 86.5 (═CH_2), 156.1 (O−CH═); B, δ 85.9 (═CH_2), 157.1 (O−CH═); C, δ 87.7 (═CH_2), 156.0 (O−CH═).

Observed Lithium-Containing Species. "LiOCH═CH_2": ^{1}H NMR (THF/benzene-d_6 2/1, 400 MHz) δ 3.31 (ill-resolved dd, 1H, ═C*H*H′), 3.67 (ill-resolved dd, $J_{H,H}$ = 1.2 Hz, ═CH*H*′), 7.00 (dd, $J_{H,H}$ = 13.4 Hz, $J_{H,H}$ = 5.2 Hz, O−CH═); ^{13}C{^{1}H} NMR (THF/benzene-d_6 2/1, 400 MHz) δ 81.6 (=CH_2), 158.7 (−CH═).

"$LiOCH_2CH_2CH$═CH_2": ^{1}H NMR (THF/benzene-d_6 2/1, 400 MHz) δ 2.19 (m, 2H, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.3 Hz, CH_2), 3.78 (t, $J_{H,H}$ = 7.2 Hz, O−CH_2), 4.85 (ddt, 1H, $J_{H,H}$ = 10.2 Hz, $J_{H,H}$ = 2.5 Hz, $J_{H,H}$ = 1.1 Hz, ═C*H*H′), 4.94 (ddt, 1H, $J_{H,H}$ = 17.2 Hz, $J_{H,H}$ = 2.4 Hz, $J_{H,H}$ = 1.3 Hz, =CH*H*′), 5.89 (m, 1H, =CH−); ^{13}C{^{1}H} NMR (THF/benzene-d_6 2/1, 400 MHz) δ 43.6 (CH_2), 65.3 (OCH_2), 114.2 (═CH_2), 138.4 (−CH═).

"$LiCH_2C_6H_5$": ^{1}H NMR (THF/benzene-d_6 2/1, 400 MHz) δ 1.66 (s, 2H, CH_2), 5.59 (m, 1H, *p*-CH Ph), 6.21 (m, 2H, *o*-CH Ph), 6.45 (m, 2H, *m*-CH Ph); ^{1}H NMR (THP/benzene-d_6 2/1, 400 MHz) δ 1.62 (s, 2H, CH_2), 5.71 (m, 1H, *p*-CH Ph), 6.32 (m, 2H, *o*-CH Ph), 6.54 (m, 2H, *m*-CH Ph); ^{13}C{^{1}H} NMR (THP/benzene-d_6 2/1, 400 MHz) δ 35.7 (CH_2), 106.2 (*p*-CH Ph), 117.5 (2 × *o*-CH Ph), 128.2 (2 × *m*-CH Ph), 161.1 (*i*-C Ph).

X-ray Structure Determination. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo K*α* radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[51,52]

The structures were solved by direct methods (SHELXS[53]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[53]). The hydrogen atom bonded to the methylene groups C1 and C8 of compound **8** and all hydrogen atoms of compound **10** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All nondisordered, non-hydrogen atoms were refined anisotropically.[53] Crystallographic data as well as structure solution and refinement details are summarized in Table SI1 (Supporting Information). XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving NMR spectra, Table SI1, giving crystal data and refinement details for the X-ray structure determinations of compounds **1**−**9**, and CIF files giving crystallographic data for **1**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) has also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-866599 for **1**, CCDC-866600 for **2**, CCDC-866601 for **3**, CCDC-866602 for **4**, CCDC-866603 for **5**, CCDC-866604 for **6**, CCDC-866607 for **7**, CCDC-866610 for **8**, and CCDC-866606 for **9**. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail: deposit@ccdc.cam.ac.uk).

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: m.we@uni-jena.de. Fax: +49 (0) 3641 948132.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the German Research Foundation (DFG, Bonn/Germany) for financial funding. F.D. is also grateful to the German Academic Exchange Service (DAAD, Bonn, Germany) for support within the International Association for the Exchange of Students for Technical Experience (IAESTE program).

■ REFERENCES

(1) Hauber, S.-O.; Lissner, F.; Deacon, G. B.; Niemeyer, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 5871−5875; *Angew. Chem.* **2005**, *117*, 6021−6025.

(2) Ruspic, C.; Harder, S. *Organometallics* **2005**, *24*, 5506−5508.

(3) Fischer, R.; Görls, H.; Westerhausen, M. *Inorg. Chem. Commun.* **2005**, *8*, 1159−1161.

(4) For reviews on arylcalcium chemistry and related topics see: (a) Harder, S. *Chem. Rev.* **2010**, *110*, 3852−3876. (b) Barrett, A. G. M.; Crimmin, M. R.; Hill, M. S.; Procopiou, P. A. *Proc. R. Soc.* **2010**, *466*, 927−963. (c) Westerhausen, M.; Langer, J.; Krieck, S.; Glock, C. *Rev. Inorg. Chem.* **2011**, *31*, 143−184. (d) Westerhausen, M. *Z. Anorg. Allg. Chem.* **2009**, *635*, 13−32. (e) Coles, M. P. *Curr. Org. Chem.* **2008**, *12*, 1220−1230. (f) Westerhausen, M.; Gärtner, M.; Fischer, R.; Langer, J.; Yu, L.; Reiher, M. *Chem. Eur. J.* **2007**, *13*, 6292−6306. (g) Westerhausen, M.; Gärtner, M.; Fischer, R.; Langer, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 1950−1956; *Angew. Chem.* **2007**, *119*, 1994−2001. (h) Westerhausen, M. *Dalton Trans.* **2006**, 4755−4768. (i) Alexander, J. S.; Ruhlandt-Senge, K. *Eur. J. Inorg. Chem.* **2002**, 2761−2774. (j) Westerhausen, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2975−2977; *Angew. Chem.* **2001**, *113*, 3063−3065. (k) Hanusa, T. P. *Coord. Chem. Rev.* **2000**, *210*, 329−367. (i) Westerhausen, M. *Coord. Chem. Rev.* **1998**, *176*, 157−210.

(5) Gärtner, M.; Görls, H.; Westerhausen, M. *Synthesis* **2007**, *5*, 725−730.

(6) Fischer, R.; Gärtner, M.; Görls, M.; Westerhausen, M. *Organometallics* **2006**, *25*, 3496−3500.

(7) Langer, J.; Görls, H.; Westerhausen, M. *Inorg. Chem. Commun.* **2007**, *10*, 853−855.

(8) Krieck, S.; Görls, H.; Westerhausen, M. *J. Am. Chem. Soc.* **2010**, *132*, 12492−12501.

(9) Fischer, R.; Gärtner, M.; Görls, H.; Yu, L.; Reiher, M.; Westerhausen, M. *Angew. Chem.* **2007**, *119*, 1642−1647; *Angew. Chem., Int. Ed.* **2007**, *46*, 1618−623.

(10) Gärtner, M.; Görls, H.; Westerhausen, M. *J. Organomet. Chem.* **2008**, *693*, 221−227.

(11) Mochida, K.; Yamanishi, T. *J. Organomet. Chem.* **1987**, *332*, 247−252.

(12) Langer, J.; Krieck, S.; Fischer, R.; Görls, H.; Westerhausen, M. *Z. Anorg. Allg. Chem.* **2010**, *636*, 1190−1198.

(13) This species was misleadingly assigned earlier on as a calcium ethenolate.[6]

(14) Langer, J.; Krieck, S.; Görls, H.; Westerhausen, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 5741−5744; *Angew. Chem.* **2009**, *121*, 5851−5854.

(15) Fischer, R.; Langer, J.; Krieck, S.; Görls, H.; Westerhausen, M. *Organometallics* **2011**, *30*, 1359−1365.

(16) Reich, H. J.; Green, D. P.; Medina, M. A.; Goldenberg, W. S.; Gudmundsson, B. Ö.; Dykstra, R. R.; Phillips, N. H. *J. Am. Chem. Soc.* **1998**, *120*, 7201−7210.

(17) Gärtner, M.; Görls, H.; Westerhausen, M. *Organometallics* **2007**, *26*, 1077−1083.

(18) Langer, J.; Görls, H.; Westerhausen, M. *Organometallics* **2010**, *29*, 2034−2039.

(19) Fischer, R.; Görls, H.; Westerhausen, M. *Organometallics* **2007**, *26*, 3269−3271.

(20) Langer, J.; Gärtner, M.; Fischer, R.; Görls, H.; Westerhausen, M. *Inorg. Chem. Commun.* **2007**, 1001−1004.

(21) Krieck, S.; Görls, H.; Westerhausen, M. *J. Organomet. Chem.* **2009**, *694*, 2204−2209.

(22) Krieck, S.; Görls, H.; Yu, L.; Reiher, M.; Westerhausen, M. *J. Am. Chem. Soc.* **2009**, *131*, 2977−2985.

(23) Hevia, E.; Mulvey, R. E. *Angew. Chem., Int. Ed.* **2011**, *50*, 6448−6450; *Angew. Chem.* **2011**, *123*, 6576−6578.

(24) For a review on ether fission by organoalkalimetal compounds see: Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 972−989; *Angew. Chem.* **1987**, *99*, 1002−1019.

(25) For NMR data of lithium ethenolates see: (a) Andrews, P. C.; Bull, S. D.; Koutsaplis, M. *New J. Chem.* **2010**, *34*, 1678−1691. (b) Wen, J. Q.; Grutzner, J. B. *J. Org. Chem.* **1986**, *51*, 4220−4224. (c) Oakes, F. T.; Yang, F.-A.; Sebastian, J. F. *J. Org. Chem.* **1982**, *47*, 3094−3097.

(26) Michel, O.; Meermann, C.; Törnroos, K. W.; Anwander, R. *Organometallics* **2009**, *28*, 4783−4790.

(27) NMR data reported earlier for calcium ethenolate[6,8,21,22] deviate from these findings and might be incorrect.

(28) Mulvey, R. E.; Blair, V. L.; Clegg, W.; Kennedy, A. R.; Klett, J.; Russo, L. *Nature Chem.* **2010**, *2*, 588−591.

(29) Clayden, J.; Yasin, S. A. *New J. Chem.* **2002**, *26*, 191−192.

(30) Fleming, I.; Mack, S. R.; Clark, B. P. *Chem. Commun.* **1998**, 713−714.

(31) Margot, C.; Matsuda, H.; Schlosser, M. *Tetrahedron* **1990**, *46*, 2425−2430.

(32) For a recent review on carbolithiation see: Hogan, A.-M. L.; O'Shea, D. F. *Chem. Commun.* **2008**, 3839−3851.

(33) This assumption is based on the following considerations. The NMR shifts for the disubstituted alkene XCa−O−CH═CH−-CaX can be crudely estimated with the help of empirical increment systems. Using the NMR data of calcium ethenolate B as a starting point, the known increments of lithium[34] instead of those of calcium were applied, since no increments or NMR data of a calcium-substituted ethene are known, but the influences of calcium and lithium are expected to be similar. The additivity of the increments of both substituents was assumed. Calculated NMR shifts of the trans isomer are δ_H 7.96 and 5.64 and δ_C 166 and 146 and of the cis isomer are δ_H 8.70 and 5.91 and δ_C 166 and 146. The observed coupling constant of 9.1 Hz in the NMR spectra makes a cis isomer more likely.

(34) Increments of the lithium substituent were taken from: Bauer, W.; Griesinger, C. *J. Am. Chem. Soc.* **1993**, *115*, 10871−10882.

(35) Stanetty, P.; Mihovilovic, M. D. *J. Org. Chem.* **1997**, *62*, 1514−1515.

(36) Köbrich, G.; Baumann, A. *Angew. Chem., Int. Ed.* **1973**, *12*, 856−858; *Angew. Chem.* **1973**, *85*, 916−918.

(37) Kennedy, A. R.; Klett, J.; Mulvey, R. E.; Wright, D. S. *Science* **2009**, *326*, 706−708.

(38) The system **7**/THF was excluded due to the extended formation of byproduct, which overlaps with the signals of toluene and prohibits proper determination of the toluene content by integrating its signals in the ^{1}H NMR spectrum.

(39) Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371−2379.

(40) Wirth, H. E.; Slick, P. I. *J. Phys. Chem.* **1962**, *66*, 2277−2279.

(41) Arnett, E. M.; Wu, C. Y. *J. Am. Chem. Soc.* **1962**, *84*, 1684−1688.

(42) Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 5320−5324.

(43) Harder, S.; Müller, S.; Hübner, E. *Organometallics* **2004**, *23*, 178−183.

(44) Harvey, M. J.; Hanusa, T. P. *Organometallics* **2000**, *19*, 1556−1566.

(45) Fischer, R.; Gärtner, M.; Görls, H.; Westerhausen, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 609−612; *Angew. Chem.* **2006**, *118*, 624−627.

(46) Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*; Thieme: Stuttgart, Germany, 2005; pp 168−174.

(47) Jander, G.; Jahr, K. F.; Schulze, G.; Simon, J. *Maßanalyse*; Walter de Gruyter: Berlin, Germany, 1989.

(48) Schlosser, M.; Ladenberger, V. *J. Organomet. Chem.* **1967**, *8*, 193−197.

(49) Gilman, H.; Zoellner, E. A.; Selby, W. M. *J. Am. Chem. Soc.* **1932**, *54*, 1957−1962.

(50) Seyferth, D.; Suzuki, R.; Murphy, C. J.; Sabet, C. R. *J. Organomet. Chem.* **1964**, *2*, 431−433.

(51) *COLLECT, Data Collection Software*; Nonius BV, Delft, The Netherlands, 1998.

(52) Otwinowski, Z.; Minor, W. Processing of X-Ray Diffraction Data Collected in Oscillation Mode. In *Macromolecular Crystallography, Part A*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: New York, 1997; Methods in Enzymology Vol. *276*, pp 307−326.

(53) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.