Synthesis and Spectroscopic Properties of Arylcalcium Halides

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The direct synthesis of activated calcium with aryl halides in tetrahydrofuran (THF) gave the following compounds of the type RCaX in fair to good yields: [MesCaI(THF)$_4$] (**1**), [(*p*-tolyl)CaI(THF)$_4$] (**2**), [PhCaI(THF)$_4$] (**3**), and [PhCaBr(THF)$_4$] (**5**). All of these "heavy Grignard reagents" contain a calcium atom in a slightly distorted octahedral environment. They must be handled at low temperatures in order to avoid ether cleavage reactions. The Ca−C bond lengths vary between 2.556(5) Å (**3**) and 2.583(3) Å (**5**). The thermal stability is enhanced when the coordination number of calcium is increased. The calcium in the seven-coordinate complex [PhCaI(THF)(DME)$_2$] (**4**) has a distorted-pentagonal-bipyramidical configuration. This complex is thermally more stable and can be handled at 0 °C. The larger coordination number results in a longer Ca−C bond of 2.621(5) Å.

Introduction

More than a century ago, organometallic chemistry experienced enormous progress due to the easy access of organomagnesium halides by Grignard via the direct reaction of alkyl and aryl halides with magnesium metal. In contrast to the subsequent broad development of organomagnesium chemistry, the organometallic chemistry of the heavier alkaline earth metals, Ca, Sr, and Ba, remained somewhat unexplored despite numerous attempts. The direct synthesis of organocalcium compounds faces several challenges, due to the low reactivity of the metal itself and the extremely high reactivity of the organocalcium compounds, which often were decomposed by subsequent reactions (Wurtz-type coupling, ether cleavage). Furthermore, the ionic metal−carbon bonds resulted in formation of products that were insoluble. Therefore, several procedures were developed in order to avoid or circumvent these difficulties.

Dialkylcalcium compounds are accessible by several preparative procedures.[1] Most commonly used are the cocondensation reaction of calcium metal atoms with alkyl halides,[2,3] the use of finely divided calcium,[2] and the metathesis reaction of calcium(II) iodide with alkylpotassium compounds.[4,5] To stabilize these highly polar calcium compounds, trimethylsilyl and/or phenyl groups have been bound to the α-carbon atoms.

The direct synthesis of arylcalcium halide in a common organic solvent was investigated by Beckmann more than a century ago.[6] The activation of calcium was accomplished by addition of small amounts of iodine. Bickelhaupt and co-workers published the synthesis of diphenylcalcium by the reaction of calcium with iodobenzene at −20°C and suggested that a Schlenk equilibrium was operative.[7] Other groups employed metal displacement reactions of dialkylmercury with calcium amalgam.[8] Also, the nature of the impurities was considered in the course of these investigations. Traces of magnesium seemed to be advantageous, whereas sodium had a retarding effect.[9,10] Furthermore, the yields in the direct synthesis of arylcalcium halides were high only in ether solution, whereas in hydrocarbons only low yields were obtained.[11]

All of these procedures gave no crystalline products, and often the organocalcium compounds were not even isolated. Identification was accomplished by derivatization reactions such as hydrolysis or reactions with polar multiple bonds (for example, with C═O bonds of ketones).

The first structural characterization of an arylcalcium derivative was reported by Hauber et al.[12] In this complex the (pentafluorophenyl)calcium unit was sterically shielded by an extremely bulky triazenide ligand with pendant aryl substituents that underwent π-arene interactions with the Ca atom. This stabilization of the unusually low coordination number of 3 leads to an extremely short Ca−C bond length of 2.50(1) Å. Oxygen-centered calcium tetrahedra were found in complexes of the constitution of [Ca$_4$(μ_4-O)(μ-Ar)$_6$], with Ar = C$_6$H$_3$-2,6-(OMe)$_2$ (Ca−C = 2.716(4)−2.785(4) Å),[13] and [Ca$_4$(μ_4-O)(μ-Ph)$_3$(μ-

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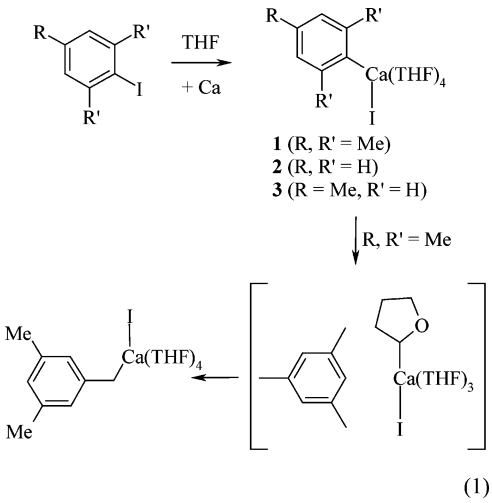
$I)_3(THF)_7]$.[14] These crystalline compounds resulted from substrate and ether cleavage reactions due to the high reactivity of the calcium−carbon bond. In these cages the aryl substituents bridge the Ca···Ca edges of the Ca_4 tetrahedra. Finally, the synthesis and structural characterization of the tetrakis(tetrahydrofuran) complex of (2,4,6-trimethylphenyl)calcium iodide (**1**) (mesitylcalcium iodide) succeeded at very low temperature and showed that this compound already decomposed above −30 °C.[15] Here we report the synthesis of unsubstituted phenylcalcium iodide and bromide as examples of heavy Grignard reagents without steric strain and their kinetic stabilization by an increase of the coordination number of the calcium atom.

Results and Discussion

Synthesis. The calcium metal was activated prior to use by dissolving in liquid ammonia and the subsequent removal of NH_3 in vacuo. The direct reaction of aryl iodides with activated calcium metal in THF at −78 °C yielded arylcalcium iodide, according to eq 1. Titration of these reaction mixtures gave



(1)

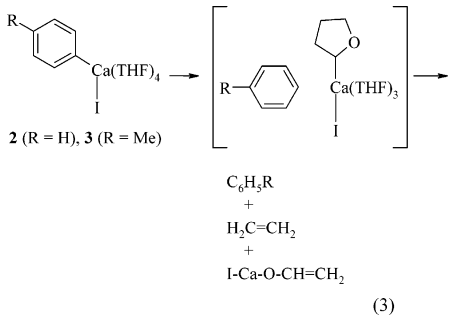
ArCaI yields above 60%. Warming the THF solution of mesitylcalcium iodide above −30 °C led to a color change:[15] Within a few hours the colorless reaction solution turned yellow, due to the formation of (3,5-dimethylbenzyl)calcium iodide according to eq 1, which can easily be identified by NMR spectroscopy. The deuteriolysis experiments with D_2O gave [D]-mesitylene with the deuterium atom at a methyl group.[15]

Kinetic investigations of the decomposition of $MesCa(THF)_4I$ (**1**) showed a process which is independent of the concentration of the ArCaI compound. However, a strong dependence on the solvent was observed. Deuteration of the solvent strongly increases the half-life, whereas higher temperatures reduced the half-life of this compound. For example, the amount of **1** decreased in a 1/9 THF/ [D_8]THF mixture at 0 °C according to eq 2 (with n_0 being the amount (or concentration) of RCaI at t

$$(n_t/n_0) \times 100 = 100 - (0.6/\text{min})t \qquad (2)$$

= 0 min and n_t being the amount (or concentration) of RCaI after the time t (in minutes)). Below concentrations of 20% of the original value the MesCaI amount was slightly higher than that calculated, and even after a few hours a very small amount of RCaI still remained. This deviation from the linear proportionality possibly may be explained by the formation of cages which contain RCaI in addition to the degradation products. In support of this idea, for phenylcalcium iodide the oxygen-centered Ca_4 cage [$(PhCaI)_3$·CaO·7THF] was found earlier in low yield, and this explains the residual phenyl substituents.[14] For mesitylcalcium iodide also the formation of (3,5-dimethylbenzyl)calcium iodide was observed.[15]

Therefore, we investigated also the degradation of tetrakis(tetrahydrofuran)(*p*-tolyl)calcium iodide (**3**) more closely in order to investigate which decomposition products can be observed. In a sealed tube the degradation of **3** in THF solution was investigated by NMR spectroscopy. This compound reacted with THF and formed toluene, ethene ($\delta(^1H)$ 5.31, $\delta(^{13}C)$ 125.8), and ethenolate ($\delta(^1H)$ 8.51 (CH, $^3J(H,H)_{trans} = 5.8$ Hz, $^3J(H,H)_{cis} = 1.8$ Hz), 6.91 and 6.68 (CH_2, $^2J(H,H) = 6.9$ Hz); $\delta(^{13}C)$ 144.2 (OCH), 126.3 (CH_2)) according to eq 3. The decrease of the



(3)

concentration followed a time dependence similar to that described for mesitylcalcium iodide. However, a remetalation and the formation of benzylcalcium iodide as found for mesitylcalcium iodide (**1**) was not observed for **3**. This fact suggests that ether cleavage occurred much more quickly than the rotation and deprotonation of the toluene molecule which was formed in the deprotonation of the THF ligand.

To increase the stability of the arylcalcium iodide, an increase of the coordination number seemed to be a feasible concept. Therefore, we added 1,2-dimethoxyethane to the THF solution of the phenylcalcium iodide species **2** and obtained $PhCaI(THF)(DME)_2$ (**4**) with a seven-coordinate calcium atom. This complex is soluble in THF and DME and less soluble in diethyl ether. Compound **4** is stable at 0 °C, whereas **2** decomposed even at −30 °C.[15]

The reaction of bromobenzene with calcium was performed at room temperature in order to maintain an acceptable reaction rate. After 3 h the yield of PhCaBr was approximately 50%. Longer reaction times resulted in a higher content of decomposition products (ether cleavage as well as formation of biphenyl due to Wurtz-type coupling reactions) but not in a higher product yield. Cooling of the reaction mixture to −90 °C resulted in crystallization of the tetrakis(tetrahydrofuran) complex of phenylcalcium bromide. The side products remained in solution. The reaction of activated calcium with chlorobenzene gave yields of less than 5% of PhCaCl. The isolation of phenylcalcium chloride failed.

NMR Spectroscopy. The proton NMR parameters are listed in the Experimental Section and are in accord with expectation. However, earlier ^1H NMR spectroscopic investigations of Fraenkel et al.[16] regarding (*p*-tolyl)calcium iodide are not in agreement with our data, which are much more similar to those for the magnesium derivative, PhMgI.

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Table 1. Comparison of the $^{13}C\{^1H\}$ NMR Spectroscopic Parameters (Chemical Shifts, THF Solution) of Arylcalcium Halides

	MesCaI-(thf)$_4$ (**1**)	PhCaI-(thf)$_4$ (**2**)	TolCaI-(thf)$_4$ (**3**)	PhCaI(thf)-(dme)$_2$ (**4**)	PhCaBr-(thf)$_4$ (**5**)
δ(*i*-C)	182.5	190.3	185.3	190.3	190.0
δ(*o*-C)	147.1	141.1	141.3	141.1	142.1
δ(*m*-C)	124.2	125.3	126.2	125.4	128.9
δ(*p*-C)	131.0	122.5	130.4	122.7	123.3
δ(*o*-Me)	27.7				
δ(*p*-Me)	21.6		21.8		
ref	15	14			

Table 2. Comparison of Selected Bond Lengths (Å) and Angles of Arylcalcium Halides[a]

	MesCaI-(thf)$_4$ (**1**)	PhCaI-(thf)$_4$ (**2**)	TolCaI-(thf)$_4$ (**3**)	PhCaI(thf)-(dme)$_2$ (**4**)	PhCaBr-(thf)$_4$ (**5**)
CN	6	6	6	7	6
Ca−C1	2.574(4)	2.574(7)	2.556(5)	2.621(5)	2.583(3)
Ca−X	3.2084(9)	3.178(3)	3.173(1)	3.192(1)	2.8899(8)
Ca−O	2.406(3)	2.38(1)	2.382(4)	2.495(3)	2.387(3)
C−Ca−X	177.4(1)	177.4(2)	174.6(1)	175.35(9)	178.51(9)
Ca−C1−C2	124.5(3)	121.9(5)	118.4(4)	122.7(3)	128.7(3)
Ca−C1−C6	121.3(3)	117.7(5)	128.4(4)	118.6(3)	117.9(3)
C2−C1−C6	114.2(4)	120.0[b]	113.2(5)	118.6(4)	113.2(3)
ref	15				

[a] Abbreviations: CN, coordination number of calcium; Mes, 2,4,6-trimethylphenyl, mesityl; Tol, *p*-tolyl; Ph, phenyl; X = I, Br. [b] The phenyl ring was restrained as a regular hexagon with equal C−C bond lengths.

The $^{13}C\{^1H\}$ NMR spectroscopic data are summarized in Table 1. The ipso carbon atoms of the phenylcalcium halides show a remarkably low field shift and are independent of the halogen atom. The substitution of the phenyl rings by methyl groups leads to a slightly high field shifted resonance. As expected, the replacement of a proton by a methyl group leads to a strong low-field shift of the corresponding arene carbon atom. Neither the halogen atom nor the coordination number of the calcium atom show an influence on the $\delta(^{13}C)$ values of the phenyl substituent.

Molecular Structures. In Table 2 selected structural parameters of the arylcalcium iodides **1**−**4** and the phenylcalcium bromide **5** are given. The single crystals of PhCaI(THF)$_4$ (**2**) became dull during handling and mounting on the diffractometer, even at temperatures below −40 °C. Therefore, we were only able to evaluate a structural motif under fixation of a regular hexagon with equal C−C bond lengths for the phenyl ring. However, this procedure limits the discussion of the structural parameters of **2**. Single crystals of **3** were isolated which could be mounted and centered on the diffractometer at very low temperatures, whereas for **4** it was sufficient to maintain temperatures of approximately 0 °C during handling and mounting. The phenylcalcium bromide **5** also was thermally more stable, and handling at −10 °C allowed mounting on the diffractometer without decomposition. The molecular structures are given in Figures 1−3, respectively, for (*p*-tolyl)CaI(THF)$_4$ (**3**), PhCaI(THF)(DME)$_2$ (**4**), and PhCaBr(THF)$_4$ (**5**).

In all hexacoordinate complexes the calcium atoms are in a distorted-octahedral environment, whereas the seven-coordinate calcium center in **4** shows a distorted-pentagonal-bipyramidal geometry. In all of these arylcalcium halides the C1−Ca−I unit is nearly linear and these compounds show a trans arrangement. The ipso carbon atoms are in planar environments. However, the Ca−C1−C(*n*) angles (n = 2, 6) differ significantly. The acute angle C2−C1−C6 is characteristic for phenyl anions,[17] and the angle becomes smaller with decreasing Ca−C1 distances. In **3** the difference of 10° between distal and proximal Ca−C1−C(*n*) angles is extremely large. Due to the fact that the calcium atom in **3** has a free coordination site, the *p*-tolyl substituent bends toward the metal cation. As expected, a higher coordination number of the Ca atom and a higher degree of coordinative saturation as in **4** or enhanced steric shielding as in **1** weaken this effect.

An increase in the intramolecular steric strain leads to an increase in the calcium−carbon bond lengths of the arylcalcium iodides. For (*p*-tolyl)Ca(thf)$_4$I (**3**) a short Ca−C1 bond of 2.556(5) Å was observed. Enhanced strain introduced by the *o*-methyl

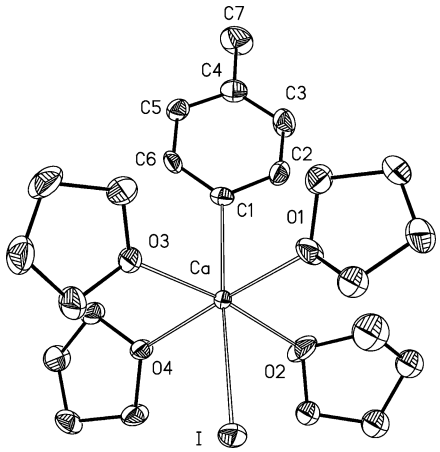

Figure 1. Presentation of the molecular structure of (*p*-tolyl)CaI(THF)$_4$ (**3**). The ellipsoids represent a probability of 40%, and all hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (deg) in the coordination sphere of Ca: Ca−O1 = 2.373(4), Ca−O2 = 2.376(4), Ca−O3 = 2.380(4), Ca−O4 = 2.399(3); C1−Ca−O1 = 88.7(2), C1−Ca−O2 = 94.8(2), C1−Ca−O3 = 91.1(2), C1−Ca−O4 = 94.8(2), O1−Ca−O2 = 90.0(2), O1−Ca−O3 = 94.1(2), O1−Ca−O4 = 176.5(1), O2−Ca−O3 = 172.9(2), O2−Ca−O4 = 90.4(2), O3−Ca−O4 = 85.2(1).

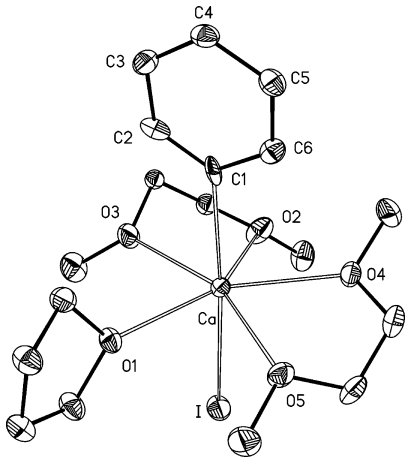

Figure 2. Presentation of the molecular structure of PhCaI(THF)(DME)$_2$ (**4**). The details are similar to those of Figure 1. Bond lengths (Å) and angles (deg) in the coordination sphere of Ca: Ca−O1 = 2.497(3), Ca−O2 = 2.486(3), Ca−O3 = 2.495(3), Ca−O4 = 2.512(3), Ca−O5 = 2.487(3); C1−Ca−O1 = 91.6(1), C1−Ca−O2 = 96.4(1), C1−Ca−O3 = 86.0(1), C1−Ca−O4 = 85.8(1), C1−Ca−O5 = 99.6(1), O1−Ca−O2 = 143.1(1), O1−Ca−O3 = 77.1(1), O1−Ca−O4 = 144.89(9), O1−Ca−O5 = 80.8(1), O2−Ca−O3 = 67.7(1), O2−Ca−O4 = 71.8(1), O2−Ca−O5 = 132.5(1), O3−Ca−O4 = 137.4(1), O3−Ca−O5 = 157.3(1), O4−Ca−O5 = 65.23(9).

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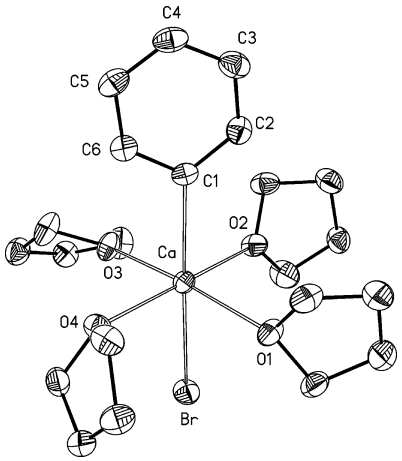

Figure 3. Presentation of the molecular structure of $PhCaBr(THF)_4$ (**5**). The details are similar to those of Figure 1. Bond lengths (Å) and angles (deg) in the coordination sphere of Ca: Ca−O1 = 2.395(3), Ca−O2 = 2.394(3), Ca−O3 = 2.364(3), Ca−O4 = 2.394(3); C1−Ca−O1 = 93.1(1), C1−Ca−O2 = 94.2(1), C1−Ca−O3 = 93.6(1), C1−Ca−O4 = 90.3(1), O1−Ca−O2 = 92.0(1), O1−Ca−O3 = 173.09(9), O1−Ca−O4 = 92.96(9), O2−Ca−O3 = 86.03(9), O2−Ca−O4 = 173.1(1), O3−Ca−O4 = 88.51(9).

groups or by enhancement of the coordination number leads to a slight elongation of the Ca−C1 bonds.

A comparison of (*p*-tolyl)$Ca(thf)_4I$ (**3**) with $PhCa(thf)_4Br$ (**5**) allows the evaluation of the influence of the halide on the structural parameters. Due to the smaller radius of bromine, the Ca−Br bond is approximately 30 pm shorter than the Ca−I distance. This leads to a slightly greater intramolecular strain and a slight lengthening of the Ca−C1 and Ca−O bonds.

Perspectives. With these arylcalcium iodides a group of heavy alkaline earth metal Grignard reagents is available. With these easily accessible reagents and the possibility to enhance their stability by addition of DME to increase the coordination number of the calcium, further development of the organocalcium chemistry can be expected. These calcium derivatives can be handled at 0 °C in common organic solvents. The organocalcium iodides as well as the bromides can be prepared in high purity.

Experimental Section

All manipulations were carried out under an anhydrous argon atmosphere. The solvents were thoroughly dried and distilled under an argon atmosphere. Compounds **1**[15] and **2**[14] were prepared according to a literature procedure. These compounds lose coordinated THF very easily once they are isolated and decompose rapidly at temperatures above 0 °C. Therefore, the analysis is limited to X-ray structure determinations, NMR spectroscopic investigations, and determination of the metal content by acid−base titrations in order to determine the yield.

Activation of Calcium. Calcium flakes and 50 g of glass balls (diameter 5 mm) were placed in a 500 mL flask and covered with liquid anhydrous ammonia. This blue solution was shaken, and the ammonia was removed in vacuo. During this procedure the flask was shaken in order to avoid the formation of metal clumps. Thereafter, the residue was dried until high vacuum was obtained. The ammonia-free metal powder remained in the flask and was used for subsequent procedures.

Large-Scale Synthesis of $PhCaI(thf)_4$ (2). In a 500 mL Schlenk flask 200 mL of THF was added to 6.39 g of activated Ca (159.4 mmol) and 100 g of glass balls (diameter 5 mm). At −10 °C 22.77 g of iodobenzene (111.6 mmol, 0.7 equiv) was added dropwise. After complete addition, the reaction was completed by shaking the reaction mixture for an additional 2 h at 0 °C. Thereafter, the reaction mixture was warmed to room temperature and filtered. The brown filtrate was cooled to −90 °C, and colorless crystals of **2** precipitated. Yield: 41.9 g of **2**, 70%. At lower temperatures, the direct synthesis occurs much more slowly, and at higher temperatures the amount of decomposition products (ether cleavage) increases. Because it was possible to purify the compound by crystallization at −90 °C, this was the best procedure. The NMR data were identical with those published earlier.[14]

Synthesis of (*p*-tolyl)$CaI(thf)_4$ (3). A 250 mL Schlenk flask containing 0.66 g of activated calcium (16.5 mmol), 60 mL of THF, and approximately 100 glass balls (diameter 5 mm) was cooled to −78 °C. Then 2.6 g of *p*-iodotoluene (11.9 mmol, 0.7 equiv) was added, and the flask was shaken for 1 h in a dry ice container. After this time the temperature was raised slowly within 3 h to 0 °C. Thereafter, the excess of calcium and the glass balls were removed with a cooled Schlenk frit. The volume of the filtrate (60% yield of organocalcium compound calculated by acid consumption by an aliquot) was reduced to half of the original volume and then kept at −78 °C. Colorless crystals of **3** (2.5 g, 38%) were collected on a cooled frit and dried in vacuo.

Crystals of **3** already became dull at −40 °C. The sensitivity was comparable to that of $MesCaI(thf)_4$ reported earlier. Spectroscopic data of **3** are as follows. ^{1}H NMR (200.1 MHz, [D$_8$]THF, 240 K): δ 7.50 (AA′BB′, 2H, *o*-C*H*), 6.60 (AA′BB′, 2H, *m*-C*H*), 2.06 (s, 3H, *p*-CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, [D$_8$]THF, 240 K): δ 185.3 (*i*-*C*), 141.3 (*o*-*C*H), 130.4 (*p*-*C*), 126.2 (*m*-*C*H), 21.8 (*p*-*C*H_3).

Synthesis of $PhCaI(thf)(dme)_2$ (4). Isolated $PhCaI(thf)_4$ (**2**) was recrystallized from 1,2-dimethoxyethane at −90 °C.

Spectroscopic data of **4** are as follows. ^{1}H NMR (400.25 MHz, [D$_8$]THF, −20 °C): δ 7.60−7.80 (m, 2H, *o*-C*H*), 6.75−7.00 (m, 2H, *m*-C*H*), 6.65−6.75 (m, 1H, *p*-C*H*). ^{13}C{^{1}H} NMR (100.64 MHz, [D$_8$]THF, −20 °C): δ 190.3 (*i*-*C*), 141.1 (*o*-*C*H), 125.4 (*m*-*C*H), 122.7 (*p*-*C*H).

Synthesis of $PhCaBr(thf)_4$ (5). Activated calcium metal (1.91 g, 47.7 mmol) and 50 g of glass balls were placed in a Schlenk flask and covered with 50 mL of THF. At room temperature 5.24 g of bromobenzene (33.4 mmol, 0.7 stoichiometric equivalents) was added dropwise. Subsequently, the reaction mixture was shaken at ambient temperature for an additional 3 h. During this time, the solution turned brown. Then all solid materials (excess of calcium, glass balls) were removed. The acidimetric titration showed a product yield of approximately 50%. Cooling of this solution to −90 °C resulted in the precipitation of single crystals of **5**, suitable for an X-ray structure determination.

Spectroscopic data of **5** are as follows. ^{1}H NMR (200.13 MHz, [D$_8$]THF, 25 °C): δ 7.80 (d, 2H, *o*-C*H*, J = 5.6 Hz), 6.81 (m, 2H, *m*-C*H*), 6.65−6.75 (m, 1H, *p*-C*H*). ^{13}C{^{1}H} NMR (50.32 MHz, [D$_8$]THF, 25 °C): δ 190.0 (*i*-*C*), 142.1 (*o*-*C*H), 128.9 (*m*-*C*H), 123.3 (*p*-*C*H).

X-ray Structure Determinations. The intensity data of **2**−**5** were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data were corrected for Lorentz−polarization and for absorption effects.[18−20] Details of the measurements of the data sets as well as of the refinement procedures are given in Table 3.

The structures were solved by direct methods (SHELXS[21]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-

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

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

(20) Blessing, R. H. SORTAV. *Acta Crystallogr., Sect. A* **1995**, *51*, 33−38.

(21) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

Table 3. Crystal Data and Refinement Details for the X-ray Structure Determinations of Compounds 3−5

	(*p*-tolyl)CaI(thf)$_4$·$^1/_4$THF (**3**)	PhCaI(thf)-(dme)$_2$ (**4**)	PhCaBr-(thf)$_4$ (**5**)
formula	$C_{23}H_{39}CaIO_4$·0.25C_4H_8O	$C_{18}H_{33}CaIO_5$	$C_{22}H_{37}BrCaO_4$
formula wt	564.55	496.42	485.51
T/K	183(2)	183(2)	183(2)
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	9.470(2)	16.685(3)	8.2421(4)
b/Å	11.888(2)	13.044(3)	35.594(2)
c/Å	12.750(3)	10.399(2)	8.3000(4)
α/deg	90.66(3)	90	90
β/deg	96.77(3)	97.63(3)	96.318(3)
γ/deg	96.70(3)	90	90
V/Å^3	1415.2(5)	2243.2(8)	2420.2(2)
Z	2	4	4
ρ/g cm^{-3}	1.325	1.470	1.332
μ/mm^{-1}	1.337	1.678	1.933
F(000)	584	1016	1024
2*θ* range/deg	4.4 < 2*θ* < 54.9	5.4 < 2*θ* < 54.9	5.6 < 2*θ* < 55.0
no. of indep rflns	6288 (R_{int} = 0.0211)	5135 (R_{int} = 0.0543)	4780 (R_{int} = 0.0359)
no. of restraints	10	0	0
no. of params	270	228	253
wR2 (all data)[a]	0.1713	0.1187	0.1120
R1 (all data)[a]	0.0773	0.0857	0.0897
R1 ($I > 2\sigma(I)$)[a]	0.0590	0.0464	0.0490
s[b]	1.025	1.013	1.002
resid dens/e Å^{-3}	+1.500/−0.689	+1.271/−1.124	+0.526/−0.463
CCDC No.	CCDC-294260	CCDC-294261	CCDC-605500

[a] Definition of the *R* indices: R1 = $(\sum||F_o| - |F_c||)/\sum F_o|$; wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. [b] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

97[22]). The crystals of **2** turned dull during handling and mounting, even below −40 °C. During the refinement procedures[23] the phenyl ring was fitted with an ideal hexagonal geometry, and no detailed discussion can be offered. Therefore, a CIF file was not deposited and a CCDC number was not ordered for this structure determination. In **3** two of the THF molecules show a two-site disordering; the disordered atoms were refined isotropically. In **4** one of the DME ligands shows a two-site disorder and the respective atoms are also considered isotropically. The hydrogen atoms were included at calculated positions with fixed thermal parameters. All other non-hydrogen atoms were refined anisotropically.[22] XP (SIEMENS Analytical X-ray Instruments, Inc.) and POVRAY were used for structure representations.

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Supporting Information Available: Listings of data collection and refinement procedures as well as positional coordinates of all atoms (CIF files) for **3**−**5**. This material is available free of charge via the Internet at http:/pubs.acs.org. In addition, the data deposited at the Cambridge Crystallographic Data Centre under CCDC-294260 (**3**), -294261 (**4**), and -605500 (**5**) contain supplementary crystallographic data, excluding structure factors; these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033; deposit@ccdc.cam.ac.uk).

OM060360G

(22) Sheldrick, G. M. SHELXL-97 (Release 97-2); University of Göttingen, Göttingen, Germany, 1997.

(23) Crystal data of **2**: $C_{22}H_{37}CaIO_4$, M_r = 532.50, triclinic, space group $P\bar{1}$, *a* = 12.793(1) Å, *b* = 14.451(1) Å, *c* = 16.094(2) Å, α = 111.675(6)°, *β* = 103.615(5)°, *γ* = 103.125(6)°, *V* = 2519.4(4) Å^3, *T* = 183(2) K, *Z* = 4, ρ_{calcd} = 1.404 g cm^{-3}, μ(Mo Kα) = 1.497 cm^{-1}.