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Heavy Grignard Reagents

Aryl Calcium Compounds: Syntheses, Structures, Physical Properties, and Chemical Behavior

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Organocalcium chemistry is still in its infancy. The direct synthesis of activated calcium and (substituted) iodobenzenes allows for the large-scale and high-yield synthesis of aryl calcium iodides. The influence of the substitution patterns of the phenyl group, halogen atom, and solvent is discussed. Aryl calcium iodides show a Schlenk equilibrium that enables the isolation of diaryl calcium derivatives. Owing to the high reactivity of aryl calcium halides, low temperatures have to be maintained throughout the preparative procedures in order to avoid side reactions. A decrease of reactivity and, hence, an enhanced stability at higher temperatures can be achieved by shielding of the calcium atom by increasing the coordination number of the metal center or by substitution of the iodide anion by bulky groups.

1. Historical Outline

Investigations regarding the organic chemistry of alkali metals date back to 1847 when Frankland treated potassium with ethyl iodide.[1] Today, various molecular structures of organoalkali-metal compounds are well-known.[2] The synthesis of the organomagnesium compounds by Grignard, who was awarded the Nobel Prize in 1912, led to a vast development of the organometallic chemistry not only of the main-group elements but also of the transition metals.[3] These organometallic compounds, especially of lithium and magnesium, proved to be very powerful as strong bases and nucleophiles as well as alkyl- and aryl-transfer reagents. The organic chemistry of the heavier alkaline-earth metals attracted far less attention. Nevertheless, attempts to prepare and isolate organocalcium compounds were undertaken and summarized by Gowenlock and Lindsell.[4] On the basis of these early attempts, Eisch and King[5] expected already 25 years ago that the potentially useful organocalcium derivatives would gain in importance. In 1974 Zerger and Stucky published the molecular structure of polymeric calcocene.[6] Thereafter, the expectations of Eisch and King were only fulfilled for the calcocene chemistry,[7] but there are only very few examples for derivatives with Ca–C σ bonds.[8]

Efforts toward preparing such compounds were intensified after isolation and determination of the molecular structure of $[Ca\{CH(SiMe_3)_2\}_2(diox)_2]$ (diox = 1,4-dioxane) by Lappert and co-workers ($d(Ca{-}C) = 248.3(5)$ pm).[9] A bent C-Ca-C unit with an angle of 149.7(6)° was found for solvent-free $[Ca\{C(SiMe_3)_3\}_2]$ ($d(Ca{-}C) = 245.9(9)$ pm).[10] The stabilization of alkyl calcium derivatives by trialkylsilyl groups at the α-carbon atom ensures solubility in common organic solvents and an effective shielding of the reactive Ca–C bonds. Alternatively, phenyl substitution also stabilizes these compounds, yielding benzylcalcium derivatives which often show a side-on coordination of the benzyl anion to the calcium center.[11,12]

Already 100 years ago, Beckmann described the first aryl calcium derivative, namely the synthesis of PhCaI in diethyl ether.[13] Thereafter, several publications on phenylcalcium halides and diphenylcalcium followed. However, these compounds remained essentially uncharacterized and their formation was concluded from derivatization reactions with ketones, aldehydes, esters, alkenes, and subsequent hydrolytic work-up procedures.[4] The incorporation of the aryl moiety into a crown ether as in 2-(phenylcalcio)-1,3-xylylene-[18]crown-5 enhanced the thermal stability, but owing to its low solubility the characterization of this compound had to be performed through derivatization.[14] The cocondensation of calcium with benzene and alkyl benzenes yielded the insertion products, namely the aryl calcium hydrides.[15] However, neither NMR data nor structural parameters have been determined. The first molecular structure of a hetero-

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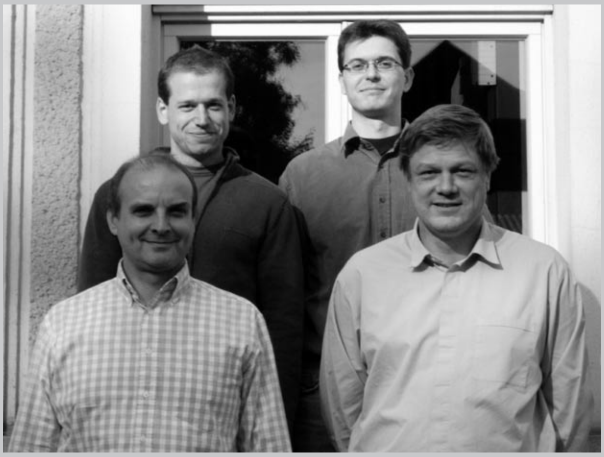
leptic organocalcium hydride was reported in 2006 by Harder et al.[16]

Recently attempts to prepare aryl calcium compounds from the metathesis reaction of CaI_2 and 2,6-dimethoxyphenylpotassium[17] and from the insertion of activated calcium into the C–I bond of iodobenzene[18] were carried out. These reactions yielded tetranuclear cage compounds of the formulas $[Ca_4\{2,6\text{-}(MeO)_2C_6H_3\}_6O]$ (av $d(\mathrm{Ca{-}C}) = 275$ pm) and $[\{CaI(Ph)(thf)_2\}_3{\cdot}CaO(thf)]$ (av $d(\mathrm{Ca{-}C}) = 259$ pm), respectively, with bridging aryl groups and central oxygen-centered Ca_4 tetrahedrons. Niemeyer and co-workers[19] employed the transmetalation of a mercury derivative and isolated a sterically shielded pentafluorophenylcalcium triazenide ($d(\mathrm{Ca{-}C}) = 249.9(11)$ pm). These complexes represent the first examples of structurally characterized aryl calcium compounds with Ca–C σ bonds.



Matthias Westerhausen (front right), born in 1959 in Nordhorn, Germany, obtained his diploma degree in 1983 from the Philipps-Universität in Marburg and a PhD in 1987 at the University of Stuttgart with Prof. Gerd Becker. He then worked as a postdoctoral fellow with Prof. Robert T. Paine at the University of New Mexico, Albuquerque. He finished his habilitation in Stuttgart in 1994 and received the venia legendi for Inorganic Chemistry in 1995. In 1996 he became professor at the Ludwig-Maximilians-Universität in Munich, serving as vice-rector from 2001 to 2004. Since 2004 he works at the Friedrich-Schiller-Universität in Jena, Germany.

Martin Gärtner (back left), born in 1980 in Blankenburg/Harz, Germany, studied chemistry at the Friedrich-Schiller-Universität in Jena. He received his diploma degree in 2005 under the supervision of Prof. Dirk Walther and is now interested in the chemistry of aryl calcium halides and their metalation and metathesis reactions.

Reinald Fischer (front left), born in 1954 in Weida/Thüringen, Germany, received his diploma degree in 1976 at the Friedrich-Schiller-Universität in Jena. He then worked at Ankerwerk Rudolstadt on the synthesis of active steroid-based substances. In 1979, he returned to the Friedrich-Schiller-Universität and obtained a PhD in 1984 with Prof. Egon Uhlig on redox reactions of organic carbonyl compounds at nickel(0) and zirconium. He then worked on the activation of CO_2 by organic nickel and zirconium compounds and has been investigating the chemistry of heavy Grignard reagents for the past two years.

Jens Langer (back right), born in 1977 in Sonneberg/Thüringen, Germany, studied chemistry at the Friedrich-Schiller-Universität in Jena and obtained a diploma degree in 2002 and a PhD in 2005 under the supervision of Prof. Dirk Walther. During this time he investigated the suitability of nickelacycles for the catalytic activation of small molecules such as carbon dioxide. He is now interested in the reactivity of heterodinuclear organometallic compounds of the heavy alkaline-earth metals.

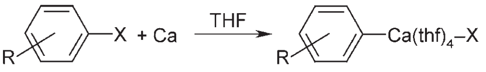
2. Challenges of Organic Calcium Chemistry

Calcium metal is less reactive than the alkali metals and magnesium and therefore, the direct synthesis of aryl calcium halides poses challenges. As a result of this fact, metal activation prior to use is necessary. The possibilities of metal activation are diverse and are summarized elsewhere.[20] Representative examples include purification by distillation,[21] activation of the alkaline-earth metals by liquid ammonia or ammonia saturation of the solvents,[22] activation with an anthracene–calcium complex (Bogdanovic method),[23] reduction of CaI_2 with potassium (Rieke procedure),[24] and the cocondensation of calcium and substrate on a refrigerated surface.[9,25]

In contrast to the low reactivity of the alkaline-earth metals, their compounds show a very high reactivity which often leads to ether-cleavage reactions.[26,27] In order to avoid these decomposition reactions, shielding of the reactive Ca–C bond and handling of the organocalcium compounds at low temperatures are advantageous. Moreover, the organic compounds of the heavy alkaline-earth metals are highly ionic and thus low solubility is often observed in common organic solvents. To increase the solubility, the calcium center has to be shielded by bulky substituents and neutral coligands such as ethers.

3. Synthesis of Aryl calcium Compounds

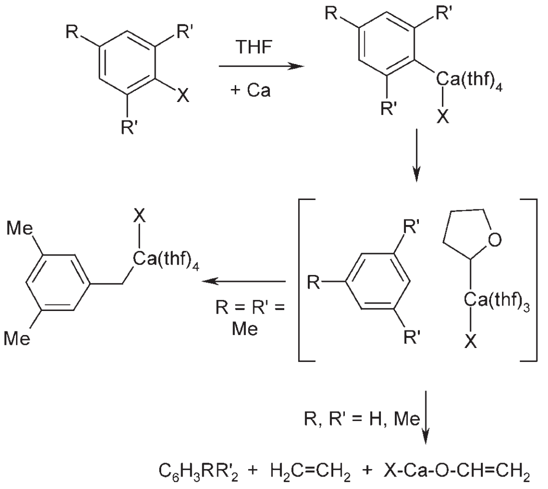
To perform the direct synthesis (insertion of calcium into a carbon–halogen bond) according to Equation (1) the calcium metal has to be activated. The alkaline-earth metal is dissolved in liquid ammonia and then all ammonia is removed immediately to avoid amide formation. Highly reactive, pyrophoric calcium powder remains in the flask[28] and is treated with iodobenzene and substituted iodobenzenes (X = I) at very low temperatures to obtain aryl calcium iodides.[28,29]



(1)

Already above −30 °C ether-cleavage reactions are observed. The α-deprotonation of the thf ligand is the initial step of the ether-cleavage reaction according to Equation (2). If methyl groups are bound to the aryl groups at the *ortho* position, a second pathway is observed; protonation at the methyl group takes place to yield yellow benzylcalcium compounds.[29]

In order to explore the scope of this direct synthesis of aryl calcium compounds, the substituents as well as the halogen

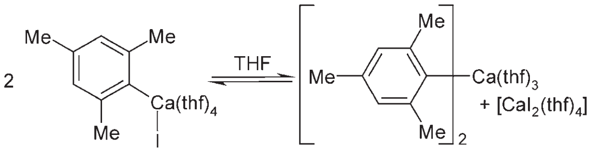


(2)

atoms of the haloarenes were varied. The yields for the reaction according to Equation (1) strongly depend on the halogen atom. The iodoarenes react readily with Ca powder whereas the yields of aryl calcium bromides are rather low and chloroarenes show nearly no reactivity toward calcium powder. At the *para* position a large variety of substituents is tolerated (such as halogen, alkyl, methoxy, dimethylamino) whereas halogen atoms at the *ortho* position lead to decomposition reactions and no 2-halogenoaryl calcium iodides can be isolated.[30] The fact that bromobenzene reacts with calcium powder is remarkable whereas no aryl calcium bromide can be isolated from the reaction of calcium with bromopentafluorobenzene, even though a heteroleptic pentafluorophenylcalcium compound is accessible by transmetalation from the corresponding mercury compound $[Hg(C_6F_5)_2]$.[19] The reaction of 1,4-diiodobenzene with calcium yields only the monoinsertion product 4-iodophenylcalcium iodide.

The $^{13}C\{^1H\}$ NMR chemical shifts of the *ipso* carbon atoms of aryl calcium halides show characteristic values between $\delta = 182$ and 190 ppm.[30] A high-field shift of the resonance is observed with methoxy or dimethylamino substituents at the *ortho* or *para* position.

Markies et al.[14] prepared diphenylcalcium at −20 °C by the direct synthesis of iodobenzene and calcium and suggested that a Schlenk equilibrium similar to that in Equation (3) is operative. The NMR spectra of 2,4,6-trimethylphenylcalcium iodide (mesitylcalcium iodide) show two sets of resonances which can be interpreted as indicating the presence of dimesitylcalcium and the heavy Grignard reagent. Cooling of the THF solutions of aryl calcium iodide to −50 °C leads to the precipitation of the tetrakis(thf) adducts of aryl calcium iodide. Further cooling to approximately −70 °C affords another crop of crystals of $[CaI_2(thf)_4]$. After removal of all iodide and reduction of the volume to an oily residue tris(tetrahydrofuran)dimesitylcalcium crystallizes at −90 °C.[31]



(3)

A solvent change to diethyl ether changes the relative solubility of the compounds involved in the Schlenk equilibrium. Cooling of this ether solution leads to the precipitation of $[Ca(Et_2O)_4I_2]$ and the solution contains mainly diaryl calcium. However, the solubility of diaryl calcium is extremely high even at very low temperatures such as −90 °C. These diaryl calcium compounds are even more reactive than the heavy Grignard reagents and ether-cleavage reactions already occur above −55 °C as, for example, for $[CaMes_2(thf)_3]$. Handling of these reaction solutions above the decomposition temperatures leads to the formation and precipitation of oxygen-centered compounds such as $[\{CaI(Ph)(thf)_2\}_3{\cdot}CaO(thf)]$[18] and $[\{Ca(Et_2O)Ph_2\}_4{\cdot}CaO(Et_2O)]$. The latter complex consists of an oxygen-centered $\{Ca_5O\}$ square pyramid of Ca atoms. All Ca···Ca edges are bridged by phenyl groups, and the ether ligands are bound terminally at the calcium atoms.

4. Structures of Aryl Calcium Compounds

The aryl calcium halides crystallize as tetrakis(thf) adducts. As a representative example the molecular structure of tolylcalcium iodide is shown in Figure 1. In all aryl calcium halides the anions are in a *trans* arrangement. The Ca–C bond lengths depend on the coordination number of the alkaline-earth-metal center. For a six-coordinate calcium center a value of 257 pm is observed, and the Ca–C distance of the seven-coordinate metal center is 262 pm.[28,29] Another characteristic feature of these molecular structures is the acute C-C-C angles at the *ipso* carbon atoms. This observation can be explained by electrostatic repulsion between the lone pair on

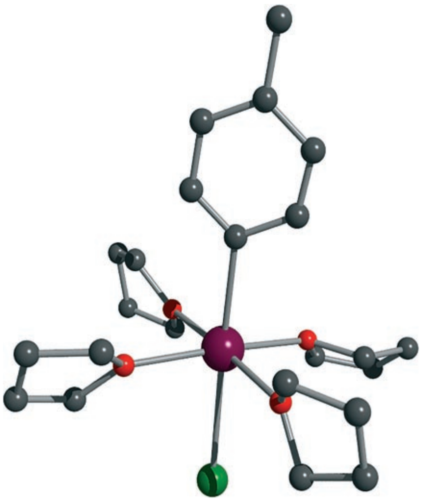


Figure 1. Molecular structure of $[CaI(thf)_4(tol)]$. The atoms are shown with arbitrary radii; H atoms are omitted for clarity. All figures employ the same color code: C black, Ca purple, Cu yellow, I green, N blue, O red, Si grey.

the *ipso* carbon atom (which carries the anionic charge) and the neighboring C–C bonds. This explanation takes into account the high heteropolar nature of the Ca–C bonds.

As the first example of a structurally characterized diaryl calcium compound the molecular structure of $[CaMes_2(thf)_3]$ (Mes = mesityl) is represented in Figure 2. The calcium center is embedded in a trigonal-bipyramidal environment with the mesityl groups in equatorial positions. The axial Ca–O bond (d(Ca–O) = 241.1(2) pm) is 4.4 pm longer than the equatorial Ca–O bonds.[31] Owing to the smaller coordination number of Ca, the Ca–C bond lengths show rather small values of 252.0(3) pm. The aryl substituent displays an acute C-C-C angle of 113.7(3)° at the *ipso* carbon atom.

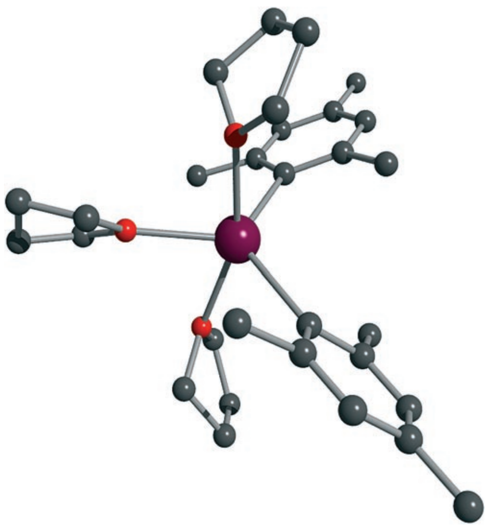


Figure 2. Molecular structure of $[CaMes_2(thf)_3]$. The atoms are shown with arbitrary radii; H atoms are omitted for clarity.

5. Reactivity Studies

Preliminary investigations regarding the reactivity of aryl calcium iodide indicate a wide field of applications. The transfer of the aryl ligand to another metal center yields the solvent-separated ions $[CaI(thf)_5]^+[VMes_4]^-$ according to Equation (4). The vanadium(III) center of the anion is in a distorted tetrahedral environment with two small (97.8°) and four large C-V-C angles (115.6°). The cation shows a distorted octahedral coordination environment at the Ca atom.[32]

To raise the stability of the aryl calcium halides, the calcium atom was shielded more effectively and the coordination number enhanced by substitution of thf ligands by 1,2-dimethoxyethane (DME) molecules. Recrystallization of $[CaI(Ph)(thf)_4]$ from DME yielded $[Ca(dme)_2I(Ph)(thf)]$ with a seven-coordinate alkaline-earth metal. Solutions of this complex underwent ether-cleavage reactions at temperatures higher than 0 °C.[28]

Another concept for stabilizing the Ca–C bonds of the aryl calcium units other than the substitution of thf by dme is the exchange of the iodide ligand by a more bulky anion. The insolubility of KI in ether solvents often is employed for the preparation of organocalcium compounds such as, for example, $[Ca\{C(SiMe_3)_3\}_2]$[10] and $[Ca_4\{2,6\text{-}(MeO)_2C_6H_3\}_6O]$.[17] Therefore, we tried to substitute the halide anion by a metathesis reaction of phenylcalcium iodide with potassium salts KX in THF at 0 °C.[33] For the reactions with X = $N(SiMe_3)_2$ and X = PPh_2 the heteroleptic complexes $[Ca\{N(SiMe_3)_2\}(Ph)(thf)_3]$ (d(Ca–C) = 253.4(3) pm) and $[Ca(Ph)(PPh_2)(thf)_4]$ (d(Ca–C) = 252.9(5) pm), respectively, are obtained in yields of more than 70%. In contrast to these findings, the performance of the metathesis reactions with potassium salts with X = C_5H_5 and X = OC_6H_2-2,6-tBu$_2$-4-Me gives the homoleptic calcocenes $[CaCp_2(thf)_2]$ and $[CaCp_2(dme)]$, depending on the solvent (THF or DME), as well as the well-known complex $[Ca(thf)_3(OC_6H_2\text{-}2,6\text{-}tBu_2\text{-}4\text{-}Me)_2]$.[34]

The molecular structure of $[Ca\{N(SiMe_3)_2\}(Ph)(thf)_3]$ is represented in Figure 3. The calcium atom is in a quasi-octahedral environment; however, the bulky bis(trimethyl silyl)amido group occupies two coordination sites, thus leading to a pentacoordinate calcium atom. The Ca–N bond length (234.7(2) pm)[33] is slightly elongated compared to those of $[Ca\{N(SiMe_3)_2\}_2(thf)_2]$ (d(Ca–N) = 229.4(3) and 230.9(3) pm)[35] and $[Ca(dme)\{N(SiMe_3)_2\}_2]$ (d(Ca–N) =

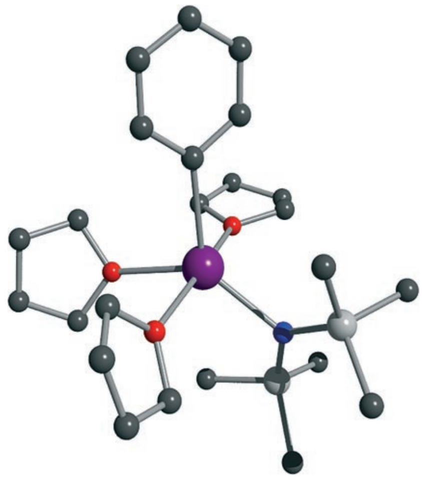
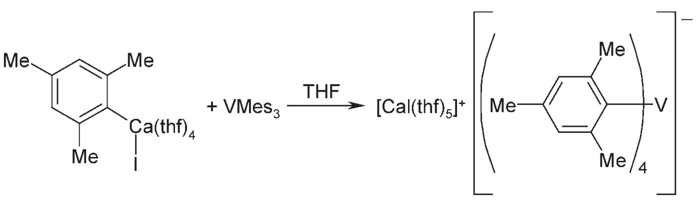


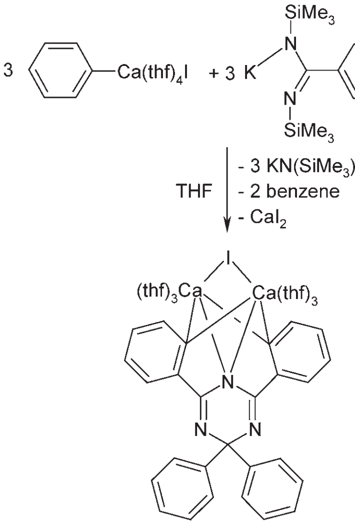
Figure 3. Molecular structure of $[Ca\{N(SiMe_3)_2\}(Ph)(thf)_3]$. The atoms are shown with arbitrary radii; H atoms are omitted for clarity.



(4)

227.1(3) pm)[36] owing to the larger coordination number of the Ca center.

The reaction of $[Ca\{N(SiMe_3)_2\}_2(thf)_2]$ with benzonitrile in THF yields bis[*N*,*N*′-bis(trimethylsilyl)benzamidinato]bis(thf)calcium.[37] The reaction of $[Ca\{N(SiMe_3)_2\}(Ph)(thf)_3]$ with benzonitrile leads to the polymerization of the nitrile; however, neither significant benzamidinate formation (reaction of PhCN with the amide ligand) nor the formation of a $Ph_2C{=}N$-Ca unit (insertion of PhCN into the Ca–C bond) is observed. In contrast to our expectation, also the metathesis reaction of $[CaI(Ph)(thf)_4]$ with potassium *N*,*N*′-bis(trimethylsilyl)benzamidinate leads to another product according to Equation (5).[33] The formation of the product can be explained by a slow liberation of benzonitrile from the *N*,*N*′-bis(trimethylsilyl)benzamidinate anion, which then was trimerized by the calcium complex with the addition of another equivalent of phenylcalcium iodide. After the *ortho* metalation the dinuclear calcium complex $[\{Ca(thf)_3\}_2(\mu\text{-}I)\{\mu,\mu\text{-}[4,4\text{-}Ph_2\text{-}2,6\text{-}(C_6H_4)_2N_3C_3]\}]$ formed with a yield of approximately 20 %. The deprotonated phenyl groups are in bridging positions between the two calcium atoms. The compounds which remain in the reaction solution undergo ligand-exchange reactions and KI precipitates with formation of $[Ca\{N(SiMe_3)_2\}_2(thf)_2]$. A trimerization of benzonitrile has been observed earlier with phenylsodium;[38] however, the subsequent *ortho* metalation seems to be characteristic for organocalcium chemistry owing to an enhanced reactivity.



(5)

The molecular structure of this product is shown in Figure 4. The *ortho*-deprotonated phenyl moieties bridge the seven-coordinate calcium atoms. Owing to the steric strain and the rather large coordination number of the calcium atoms, long Ca–C and Ca–N bonds are observed (d(Ca–C) = 265.7(7) and 269.4(7) pm; d(Ca–N) = 250.2(8) and 251.2(8) pm).[33]

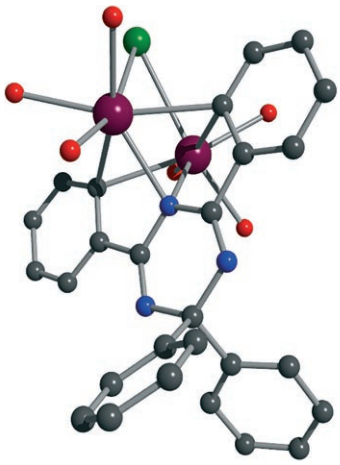
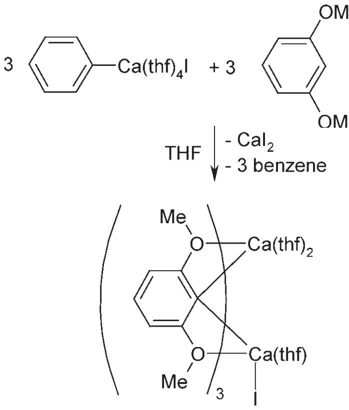


Figure 4. Molecular structure of $[\{(thf)_3Ca\}_2(\mu\text{-}I)\{\mu,\mu\text{-}[4,4\text{-}Ph_2\text{-}2,6\text{-}(C_6H_4)_2N_3C_3]\}]$. The atoms are shown with arbitrary radii; all H atoms and the carbon atoms of the thf ligands are omitted for clarity.



(6)

The metalating strength of $[CaI(Ph)(thf)_4]$ is also shown in the reaction with 1,3-dimethoxybenzene according to Equation (6).[31] The reaction of $KC_6H_3\text{-}2,6\text{-}(OMe)_2$ with CaI_2 yields the oxygen-centered Ca_4 cage compound $[Ca_4\{2,6\text{-}(MeO)_2C_6H_3\}_6O]$,[17] and the direct synthesis from activated metallic calcium gives $2,6\text{-}(MeO)_2C_6H_3CaI$ with a yield of only 56 %. The presence of the methoxy groups leads to a directed metalation of $1,3\text{-}(MeO)_2C_6H_4$ with phenylcalcium iodide at the 2-position and the formation of $[\{Ca(thf)_2\}\{CaI(thf)\}\{\mu,\mu,\mu\text{-}[2,6\text{-}(MeO)_2C_6H_3]_3\}]$,[31] the molecular structure of which is represented in Figure 5. The calcium atoms are in different environments and only the phenyl groups (d(Ca–C) = 261.3(6)–275.0(6) pm) are in bridging positions whereas the iodide ligand is bound terminally. The methoxy units are bound to the alkaline-earth-metal atoms as well and stabilize the bridging positions of the phenyl substituents. Thus, a large coordination number of eight is realized for the calcium atoms.

6. Summary and Perspectives

The field of organocalcium chemistry stands at its beginning. The large-scale and high-yield synthesis of aryl calcium iodide now opens the area of organocalcium chemistry.[28–30] However, low temperatures have to be maintained in order to

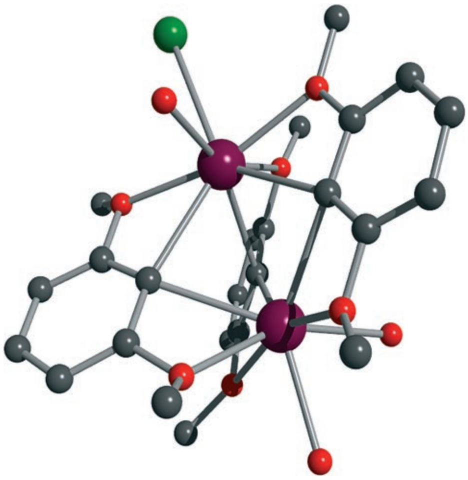


Figure 5. Molecular structure of $[\{Ca(thf)_2\}\{CaI(thf)\}\{\mu,\mu,\mu\text{-}[2,6\text{-}(MeO)_2C_6H_3]_3\}]$. The atoms are shown with arbitrary radii; all H atoms and the carbon atoms of the thf ligands are omitted for clarity.

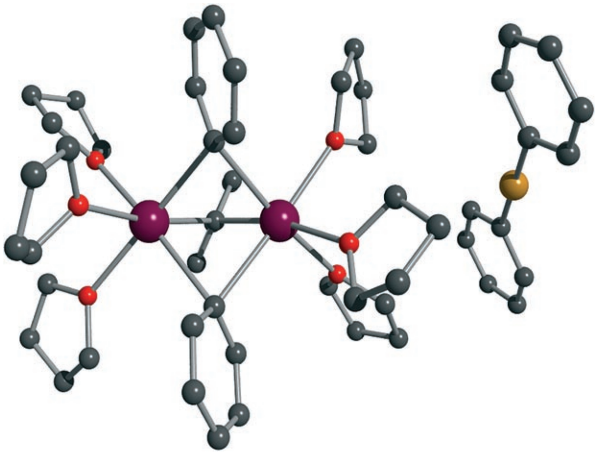


Figure 6. Molecular structure of the solvent-separated ions $[(thf)_3Ca(\mu\text{-}Ph)_3Ca(thf)_3]^+[Ph\text{-}Cu\text{-}Ph]^-$. The non-hydrogen atoms are shown with arbitrary radii; H atoms are omitted for clarity.

avoid decomposition through ether-cleavage reactions. High yields can only be obtained for the aryl calcium iodides whereas lower yields are observed for the bromides. No significant amounts of aryl calcium chlorides are available by this procedure. Furthermore, the preparation of alkyl calcium halides by the direct synthesis of activated calcium with alkyl halides poses unsolved challenges; Wurtz-type coupling compounds and CaX_2 were obtained as major products. Probably, alternate preparative methods would be more promising, such as, for example, metathesis,[10] cocondensation,[9] or transmetalation reactions.[39] Calcium readily reacts with dialkyl zinc to trialkyl zincates of the type $[Ca(ZnR_3)_2]$.[40] However, the liberation of dialkyl calcium from these zincates is not possible. The transmetalation of phenylcopper yields the solvent-separated ions $[(thf)_3Ca(\mu\text{-}Ph)_3Ca(thf)_3]^+[Ph\text{-}Cu\text{-}Ph]^-$ with hexacoordinate calcium atoms ($d(Ca{-}C) = 260.5(3)$–$262.5(2)$ pm).[41] The ionic nature of this compound, which is displayed in Figure 6, resulted in insolubility in common organic solvents.

The application of the preparative protocol on the synthesis of aryl strontium and aryl barium compounds appears promising. However, these heavy alkaline-earth metals form the alkaline-earth-metal diamides $Sr(NH_2)_2$ and $Ba(NH_2)_2$ in liquid ammonia much more easily and faster than calcium.[42] Therefore, the tendency of organic compounds of strontium and barium to contain nitrogen anions seems to be higher, which could lead to the formation of nitrogen-centered cages. The reactivity of aryl strontium and aryl barium compounds is slightly more enhanced than that of the calcium derivatives. Therefore, oxygen-centered cages such as in $[\{BaPh_2(thf)_2\}_4{\cdot}BaO(thf)]$ with bridging phenyl groups ($d(Ba{-}C) = 301(1)$–$328(1)$ pm) are found.[32] In this cage compound the central structural fragment consists of an oxygen-centered Ba_5 square pyramid. The edges of the basal square plane are bridged by phenyl groups. Moreover, the triangular planes are capped by phenyl units as well. This barium derivative shows that a Schlenk equilibrium is also operative in this case. In contrast to the corresponding reactions observed in calcium chemistry, an iodine-free cage compound is isolated from THF solution.

These organic alkaline-earth-metal compounds offer two new perspectives: Owing to the low reactivity of the calcium metal, 1,4-diiodobenzene reacts only once with activated calcium to yield $[CaI(IC_6H_4)(thf)_4]$ even in the presence of excess of calcium powder[30] whereas diiodobenzene is able to react twice with magnesium shavings[43] or lithium reagents.[44] On the other hand, the reactivity of the aryl calcium halides seems to be enhanced compared to the magnesium derivatives. This fact can be utilized for a wide field of applications such as metalation, metathesis, and addition reactions, which are under investigation in our research group. An example of enhanced reactivity has already been shown for alkaline-earth-metal phosphanides, which show some chemical similarities to the carbon analogues owing to the diagonal relationship in the periodic table.[45] Whereas $Mg[P(SiMe_3)_2]_2$ only adds to one C≡C bond of diphenylbutadiyne,[46] the derivatives of calcium, strontium, and barium undergo subsequent reactions to form phospholides (phosphacyclopentadienides).[46,47]

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