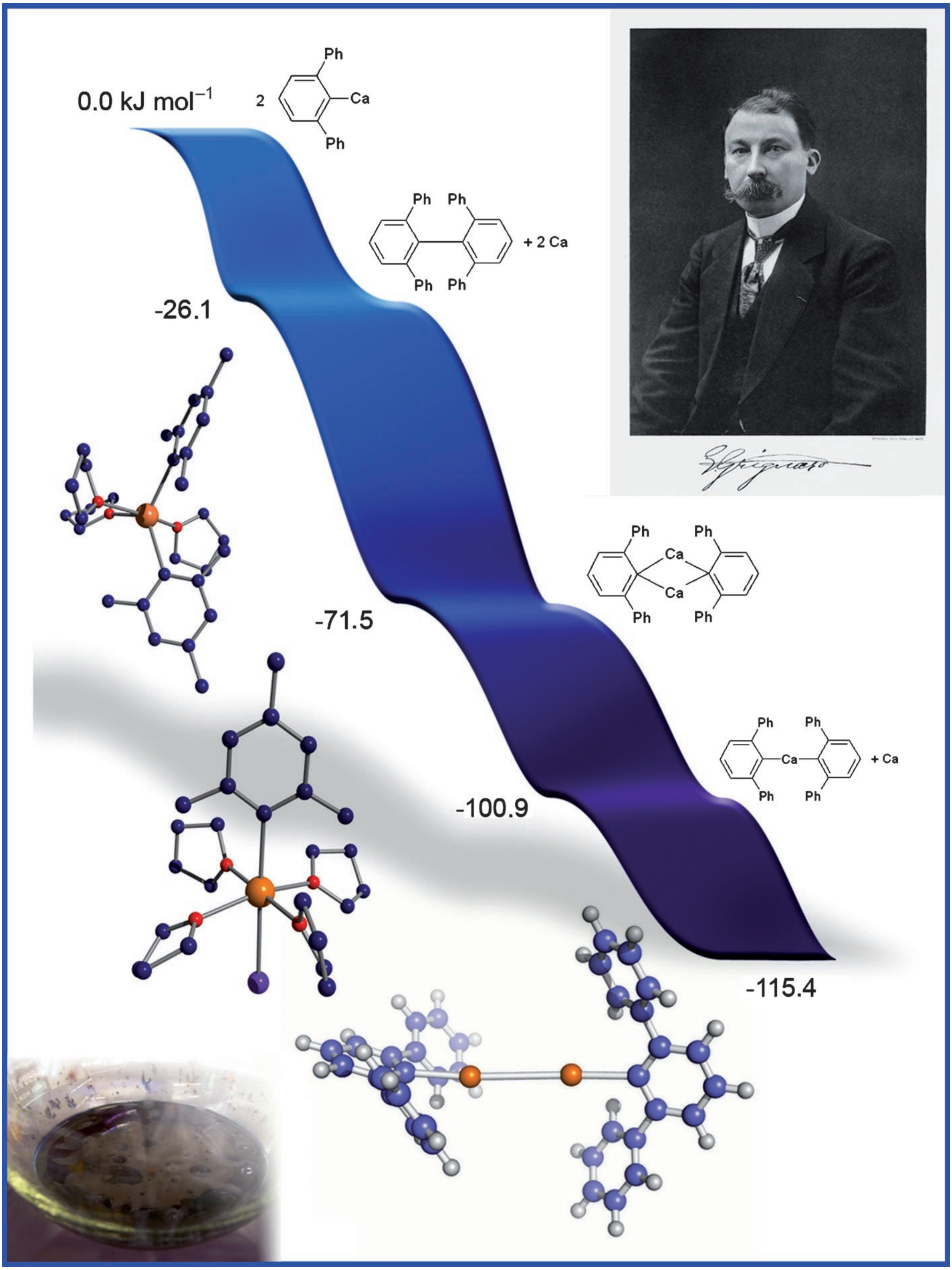
CHEMISTRY
A EUROPEAN JOURNAL

CONCEPTS

DOI: 10.1002/chem.200700558



Heavy Grignard Reagents: Challenges and Possibilities of Aryl Alkaline Earth Metal Compounds

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Abstract: Compounds of the type aryl−M−X, with M = Ca, Sr, Ba and X as any kind of ligand (such as halide, phosphanide, amide, aryl), are presented. The low reactivity of the heavy alkaline earth metals calcium, strontium, and barium enforces an activation prior to use for the direct synthesis. The insertion of these metals into C−I bonds of aryl iodides (direct synthesis) yields aryl metal iodides and has to be performed at low temperatures and in THF. Aryl alkaline-earth-metal compounds show some characteristics: 1) the ease of ether cleavage enforces low reaction temperatures, 2) for Sr and Ba the Schlenk equilibrium is shifted towards homoleptic MI_2 and MPh_2, 3) high solubility of diaryl alkaline-earth-metal derivatives in THF even at low temperatures initiated quantum chemical investigations on the aggregation behavior, and 4) a strong low field shift of the ^{13}C resonances of the *ipso* carbon atoms in NMR spectra was observed. First results from quantum chemical calculations on diaryl dicalcium(I) suggest a long Ca−Ca bond with a considerable Ca−Ca bond dissociation energy. Initial results on a selection of applications such as metallation, metathesis, and addition reactions of aryl calcium compounds are presented as well.

Keywords: alkaline earth metals • calcium • direct synthesis • Grignard reaction • organocalcium chemistry

Introduction

The early main-group organometallic chemistry dates back to the middle of the 19th century when Frankland reacted potassium[1] and zinc[2] with ethyl iodide. These organometallic compounds react violently with oxygen and the inert gas atmosphere consisting of hydrogen gas (argon and the Linde process for the isolation of nitrogen from air were unknown at that time). Shortly thereafter, Wanklyn prepared the first ethyl magnesium compounds.[3] In 1900 Grignard presented his discovery that organic magnesium compounds are easily accessible through the direct synthesis of organic halides with magnesium metal and in 1912 he was awarded with the Nobel prize (Figure 1).[4] Shortly thereafter, a vast development of the organomagnesium chemistry began, because such compounds proved to be very effective and powerful as strong bases and nucleophiles, as well as alkyl and aryl transfer reagents.[3,5–8]

First attempts to prepare alkyl and aryl calcium halides date back to 1905 when Beckmann reacted calcium metal with alkyl and aryl halides.[9] However, a repetition of these reactions showed that the major product consisted of the diethyl ether complex of calcium diiodide.[10] Working in the field of organic chemistry of the heavy alkaline earth metals calcium, strontium, and barium, researchers were often faced with difficulties and challenges, such as 1) the discrepancy between the low reactivity of the metal and the high reactivity of the organic calcium compounds, 2) side reactions due to the nucleophilicity of the organocalcium derivatives, 3) the extreme sensitivity towards moisture and air, and 4) insolubility due to highly ionic metal–carbon bonds. However, already Gilman and Schulze[10] noticed a considerable solubility of aryl calcium iodides. Despite these early investigations, the organic chemistry of the heavier alkaline earth metals attracted far less attention up to today. Nevertheless, many attempts were undertaken to prepare organocalcium compounds; however, these compounds remained essentially uncharacterized and their formation was concluded from derivatization reactions and hydrolytic workup pro-

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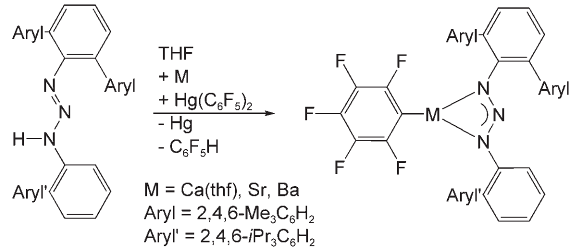
V. Grignard

Figure 1. Victor Grignard (1871–1935) was awarded in 1912 with the Nobel prize for the development of a procedure for the synthesis of RMgX from RX and Mg (Foto Deutsches Museum, Bildstelle).

cedures.[11] The early expectation of Eisch and King[12] more than 25 years ago that the potentially useful organocalcium derivatives would gain in importance remained largely unrealized. The metallocenes of calcium, strontium, and barium were an exception. After the determination of the molecular structure of polymeric calcocene by Zerger and Stucky in 1974,[13] the properties of these compounds were explored in depth.[14]

In contrast to the metallocenes, the organic chemistry of the heavy alkaline earth metals with Ca−C σ bonds remained neglected due to preparative difficulties. However, after isolation and determination of the molecular structure of $[Ca\{CH(SiMe_3)_2\}_2(diox)_2]$ by Lappert and co-workers (Ca−C 248.3(5) pm),[15] organocalcium chemistry experienced a rapid growing interest.[16,17] Solvent-free $[Ca\{C(SiMe_3)_3\}_2]$ (Ca−C 245.9(9) pm)[18] has a bent C-Ca-C unit with a bond angle of 149.7(6)°. The trialkylsilyl groups shielded the reactive Ca−C bond, ensuring reduced reactivity and enhanced solubility in common organic solvents. A similar effect could be achieved by phenyl groups in α-positions yielding benzylcalcium derivatives.[19–21]

In contrast to this tremendous success in preparing alkyl calcium derivatives, the synthesis of aryl calcium compounds remained challenging up to very recently.[17] To raise the stability of aryl calcium compounds, the aryl moiety was incorporated into a crown ether such as 2-(phenylcalcio)-1,3-xylylene[18]crown-5; however, this sparingly soluble compound had to be characterized by derivatization reactions.[22] The co-condensation of calcium with benzene and alkylbenzenes yielded the insertion products, namely the arylcalcium hydrides.[23,24] However, neither NMR data nor structural parameters were reported.[25] Only very recently, Harder published the first molecular structure of a heteroleptic organocalcium hydride.[26] Niemeyer and co-workers[27] prepared pentafluorophenyl alkaline-earth-metal derivatives from the mercury compound and employed an effective steric shielding of the Ca−C unit by bulky triazenide ligands (Ca−C 249.9(11) pm) as shown in Scheme 1.



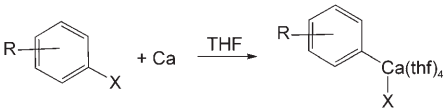
Scheme 1.

In this contribution, we will present the preparation of aryl calcium compounds as well as of the heavier homologous alkaline earth metals. Furthermore, properties and the first results of the reactivity studies of these heavy Grignard reagents will be discussed and first applications will also be presented.

Synthesis of Arylcalcium Compounds

Metal activation: In contrast to the expectations, calcium metal shows a lower reactivity than magnesium turnings and the alkali metals. Therefore, the direct synthesis of aryl calcium halides poses challenges and an activation of the alkaline earth metal prior to use is necessary. In addition, the reactivity of the metal varies depending on the purity and the trace elements, such as sodium or magnesium.[28] A purification by distillation was often employed;[29] however, the surface of crystalline calcium is rather small. To enhance the surface and to obtain highly reactive calcium powders, several procedures are suitable and have been summarized previously.[30] The activation of calcium, strontium, and barium succeeds smoothly in liquid ammonia or in ammonia-saturated solvents.[31] Further possibilities resemble the activation by decomposition of an anthracene calcium complex in hot toluene,[32] reduction of CaI_2 with potassium,[33] and the co-condensation of alkaline earth metal and substrate on a refrigerated surface.[15,34] The necessity of metal activation can be avoided by employing the metathesis reaction of calcium diiodide with organopotassium compounds, utilizing the insolubility of KI in common organic solvents.[18,19]

Direct synthesis: To insert calcium into a halogen–carbon bond (direct syntheses), the calcium must be activated. For this purpose, the alkaline earth metal is dissolved in liquid ammonia and then, all ammonia is removed immediately in order to avoid amide formation. Highly reactive and pure calcium powder remains in the flask.[35] However, for strontium and barium the amides $Sr(NH_2)$ and $Ba(NH_2)_2$ form much more easily and amide traces cannot be avoided completely.[36] At low temperatures the calcium powders react with iodoarenes and the heavy Grignard reagents can be obtained in good yields.[35,37,38] Whereas activated calcium reacts smoothly with iodobenzene in THF yielding $[CaI(Ph)(thf)_4]$[39] prolonged reaction times and lower yields are obtained for bromobenzene (Scheme 2).[38] Calcium powder shows no reactivity towards chlorobenzene. Furthermore, many substituents such as halogen, methoxy, methyl, and dimethylamino are tolerated in *para* position. However, halogen atoms in *ortho* positions lead to decomposition of the aryl calcium derivatives. Therefore, pentafluorophenyl calcium derivatives are only stable in the presence of very bulky groups in order to suppress degradation reactions.[27] Surprisingly, calcium powder reacts only once with 1,4-diiodobenzene in THF yielding the tetrakis(tetrahydrofuran) complex of 4-iodophenyl calcium iodide,[38] whereas doubly lithiated[40] and magnesiated[41] benzene was accessible.



Scheme 2.

Also the tetrakis(tetrahydrofuran) complex of naphthyl calcium iodide can be prepared by direct synthesis.[38] The molecular structure of this compound is displayed in Figure 2 and slight distortions were observed due to steric repulsion between the naphthyl group and the calcium-bound THF molecules.

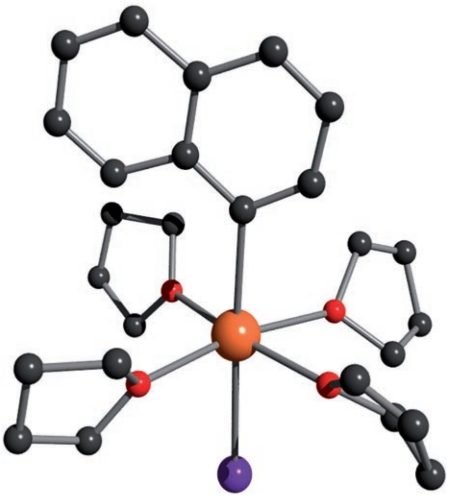
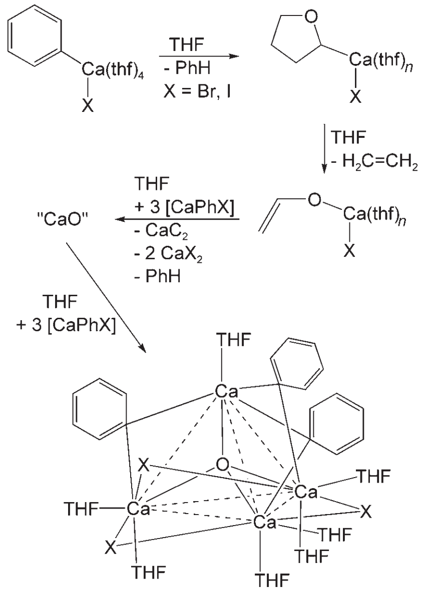


Figure 2. Molecular structure of tetrakis(tetrahydrofuran) naphthyl calcium iodide (color code: alkaline earth metal orange, I violet, O red, C black). Hydrogen atom atoms are omitted for clarity reasons.

Another crucial feature is the solvent which is chosen for the direct synthesis. Best results with respect to reaction time and yield are obtained in THF. In diethyl ether the reaction is slower, whereas in aliphatic and aromatic hydrocarbons no reaction takes place. Therefore, solvent-free aryl calcium halides were not accessible by this protocol. Furthermore, it was not possible to remove all neutral co-ligands, such as THF and Et_2O, in vacuum from the ether adducts of the aryl calcium halides.

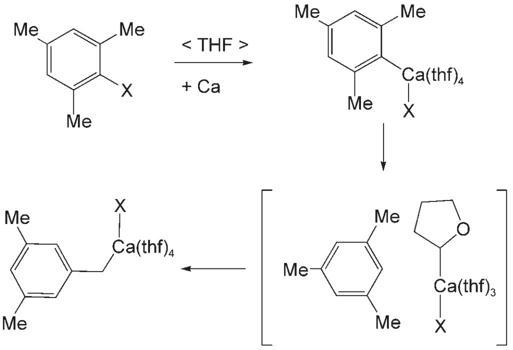
Ether cleavage: In contrast to the low reactivity of the alkaline earth metals, their organometallic compounds show a very high reactivity that often leads to ether cleavage reactions.[21,42] Therefore, maintenance of a low-temperature is necessary in order to avoid these degradation reactions. The first attempts to isolate aryl calcium compounds from the metathesis reaction of CaI_2 and 2,6-dimethoxyphenylpotassium[43] and from the insertion of activated calcium into a C–I bond of iodobenzene[39] yielded tetranuclear cage compounds of the formula $[Ca_4O\{2,6\text{-}(MeO)_2C_6H_3\}_6]$ and $[\{CaI(Ph)(thf)_2\}_3{\cdot}CaO(thf)]$, respectively, with the aryl groups in bridging positions and oxygen atoms in the center of the Ca_4 tetrahedrons. To shift the Schlenk equilibrium of $\{CaI(Ph)(thf)_4\}$ towards the homoleptic compounds $CaPh_2$ and CaI_2, the THF ligands can be removed at low temperatures and the residue can then be dissolved in Et_2O. In addition, oxygen-centered $[\{Ca(Ph)_2(Et_2O)\}_4{\cdot}CaO(Et_2O)]$ with a central Ca_5 square-pyramidal calcium cage has also been isolated.[44]

An investigation to verify whether the ether cleavage reaction was occurred by hydrolysis from traces of moisture has been undertaken. Several samples of different aryl calcium iodides in THF were stored at 0°C or room temperature for several days. The degradation of aryl calcium iodide was followed by NMR spectroscopy in a sealed NMR tube.[38] From these investigations several degradation steps have been identified. The first reaction step is the deprotonation of THF in an α-position. Thereafter, a rearrangement follows and the liberation of ethylene is observed (^{1}H NMR, $[D_8]$THF: $\delta = 5.31$ ppm; ^{13}C NMR: $\delta = 125.8$ ppm). Simultaneously calcium-bound ethenolate is formed, also detected by NMR spectroscopy {^{1}H NMR, $[D_8]$THF: $\delta = 8.51$ (dd, $J_{trans} = 5.8$ Hz, $J_{cis} = 1.8$ Hz, Ca-OCH), 6.91 (dd, $J_{gem} = 6.9$ Hz, $J_{trans} = 5.8$ Hz, CH_2), 6.68 ppm (dd, $J_{gem} = 6.9$ Hz, $J_{cis} = 1.8$ Hz, CH_2); ^{13}C NMR: $\delta = 126.3$ (CH_2), 144.2 ppm (OCH)}. Within several days the amount of ethenolate stagnates or even decreases. Parallel to these reactions the oxygen-centered cage compounds precipitate from solutions of the samples in THF. To identify the missing side products, addition of chlorotrimethylsilane to the reaction solution leads to the identification of all soluble products by mass spectrometry after chromatographic separation. Besides expected products such as benzene and phenyltrimethylsilane, bis(trimethylsilyl)acetylene is found, which suggests the formation of CaC_2 in course of the degradation of aryl calcium iodides in THF. This reaction sequence is shown in Scheme 3.



Scheme 3.

Attempts to enhance the stability of aryl calcium halides by shielding of the reactive Ca–C bond with alkyl groups in *ortho* position failed. 2,4,6-Trimethylphenyl calcium iodide can be prepared according to the procedure described above. However, already at temperatures below 0 °C degradation and ether cleavage is observed. In addition, the reaction mixture turns yellow. NMR spectroscopic investigations confirm a second minor pathway besides the ether degradation.[37] Deviating from Equation (3), the α-deprotonated THF ligand attacks the just formed mesitylene at a methyl group yielding Scheme 4. In solutions of 4-methylphenyl calcium iodide (tolyl calcium iodide) the formation of benzyl calcium moieties is not observed.



Scheme 4.

In experiments to reduce the tendency to cleave ether, the calcium center was shielded more effectively by raising the coordination number. The reaction of $[CaI(Ph)(thf)_4]$ with 1,2-dimethoxyethane (DME) yields $[Ca(dme)_2I(Ph)(thf)]$ with a seven-coordinate calcium center.[35] Solutions of this complex are stable up to 0 °C, whereas the THF adduct undergoes ether cleavage reactions already above −30 °C.

Ether cleavage is not confined to organic compounds of the heavy alkaline earth metals. The direct synthesis of mesityl magnesium bromide in diethyl ether and the dismutation after addition of 1,4-dioxane yields monomeric $[Mg(diox)_2(Mes)_2]$ as the major product; however, as a minor component also $[Mg\{EtO\text{-}CH(Me)\text{-}CH(Me)\text{-}OEt\}(Mes)_2]$ has been isolated.[45] Here the hydrogen abstraction also occurs at the α-carbon atom and a recombination of two radicals gives bidentate 2,3-diethoxybutane. The molecular structure of this magnesium complex is depicted in Figure 3.

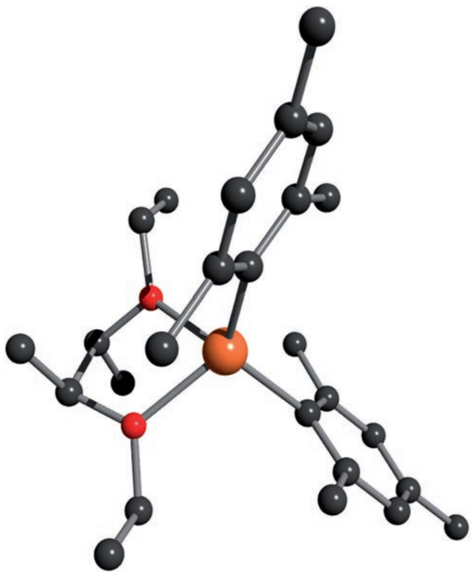


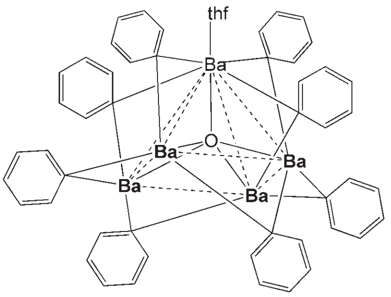
Figure 3. Molecular structure of $[Mg\{EtO\text{-}CH(Me)\text{-}CH(Me)\text{-}OEt\}(Mes)_2]$ (color code see Figure 1). H atoms are neglected due to clarity reasons.

In contrast to monomeric $[Mg(diox)_2(Mes)_2]$, dioxane addition to diphenylmagnesium leads to the precipitation of polymeric $[Mg(diox)Ph_2]_\infty$, which was extracted with hot toluene from the magnesium dihalides.[46]

The synthesis of aryl strontium and barium compounds is similar to that of the aryl calcium derivatives; however, the reactivity is slightly enhanced relative to the calcium compounds. Therefore, the oxygen-centered barium derivative $[\{Ba(thf)_2Ph_2\}_4 \cdot BaO(thf)]$ with bridging phenyl groups can be isolated; the Ba–C bond lengths vary between 301(1) and 328(1) pm (Scheme 5). The central core consists of an oxygen-centered square-pyramidal Ba_5 cage.[45]

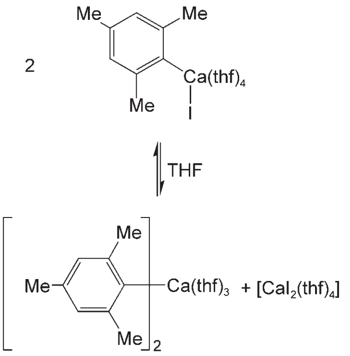
Properties of Aryl Calcium Compounds

Schlenk equilibrium: The NMR spectra of solutions of 2,4,6-trimethylphenyl calcium iodide (mesityl calcium iodide) in THF show two sets of resonances, suggesting a Schlenk equilibrium.[37] Fractional crystallization from these solutions at −50 °C and −70 °C gives crystals of $[CaI(Mes)(thf)_4]$ and



Scheme 5. Schematic drawing of $[\{\mathbf{Ba}Ph_2(thf)_2\}_4 \cdot (thf)BaO]$, the THF molecules coordinated at the bold Ba atoms are neglected for clarity reasons.

then $[CaI_2(thf)_4]$ (Scheme 6). Removal of all iodide, reduction of the volume to an oily residue, and storage at −90 °C leads to the crystallization of $[Ca(Mes)_2(thf)_3]$.[47] This organocalcium derivative is even more reactive than the aryl calcium iodides and ether cleavage occurs at temperatures above −55 °C, most probably due to a lower coordination number of five for the calcium atom. The weakly bound iodide leads to an enhanced attraction between the calcium cation and the aryl anion. The substitution of the iodide by another aryl ligand leads to two equal Ca−C bonds, which are more reactive than in arylcalcium iodides.



Scheme 6.

A solvent change from THF to diethyl ether changes the relative solubility of the compounds involved in the Schlenk equilibrium. Cooling of this solution leads to the precipitation of $[Ca(Et_2O)_4I_2]$. The solution contains mainly diaryl calcium; however, the solubility is very high even at very low temperatures such as −90 °C.

To reduce the solubility two concepts have been investigated. The choice of a triphenylsilyl group in the *para* position of the phenyl substituent lowers the solubility.[48] The insertion of Ca into the C−I bond yields a sparingly soluble compound $[CaI(4\text{-}Ph_3Si\text{-}C_6H_4)(thf)_4]$. Another possibility of lowering the solubility is offered by the synthesis of multiply metallated aryl compounds. Compound $[\{CaI(thf)_4\}_2\{(4\text{-}C_6H_4)_2Me_2Si\}]$, shown in Figure 4, was prepared by the direct synthesis. The homologous compound $[\{MgBr(thf)_4\}_2\text{-}\{(4\text{-}C_6H_4)_2Me_2Si\}]$ has been employed in a metathesis reaction with dichlorodiphenylstannanes to synthesize macrocycles of the formula $(\text{-}SiMe_2\text{-}C_6H_4\text{-}SnPh_2\text{-}C_6H_4\text{-})_3$.[49] Ether cleavage reactions of $[\{CaI(thf)_4\}_2\{(4\text{-}C_6H_4)_2Me_2Si\}]$ yielded $[CaI(thf)_4\{(4\text{-}C_6H_4)PhMe_2Si\}]$ and finally dimethyldiphenylsilane.

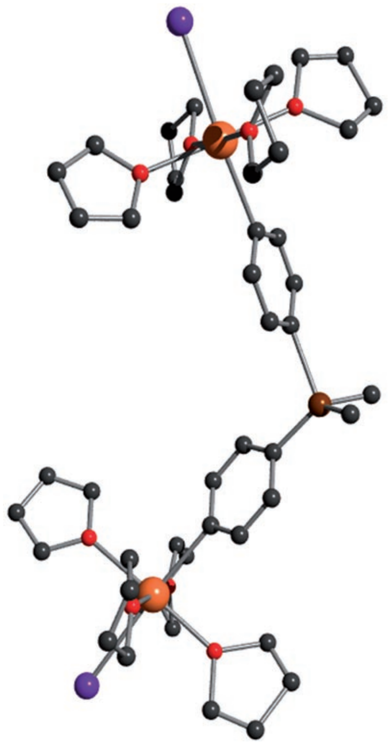


Figure 4. Molecular structure of $[\{CaI(thf)_4\}_2\{(4\text{-}C_6H_4)_2Me_2Si\}]$ (color code see Figure 1, Si brown). Hydrogen atoms are neglected for clarity reasons.

The solutions of homologous phenyl strontium and barium iodide in THF show a Schlenk equilibrium that can be shifted towards the homoleptic THF complexes of MPh_2 and MI_2. The complexes $[MI_2(thf)_5]$ precipitate upon cooling the reaction mixtures, thus shifting the Schlenk equilibrium towards the homoleptic diphenyl alkaline-earth-metal derivatives. Due to the enormous solubility of these diphenyl metal derivatives in THF only oxygen-centered cages such as $[\{BaPh_2(thf)_2\}_4 \cdot BaO(thf)]$ crystallize from these solutions.

NMR investigations: For calcium the Schlenk equilibrium lies on the side of heteroleptic CaIPh, whereas for M = Sr and Ba homoleptic MPh_2 and MI_2 are the major components. The aryl compounds of the heavy alkaline earth metals calcium, strontium, and barium show a characteristic low-field shift of the *ipso* carbon atoms of approximately $\delta = 190$, 195, and 210 ppm, respectively, in the $^{13}C\{^1H\}$ NMR spectrum.[38] Substituents such as methyl, methoxy, dimethylamino, and halogeno in the *para* position lead to a high-field shift of this resonance of up to 20 ppm, whereas silyl groups cause a slight down-field shift.[48] Methoxy groups in the 2,6-positions shift the $^{13}C\{^1H\}$ NMR signal of the calcium derivative to a value of $\delta = 152$ ppm.[38,47]

Molecular structures: The tetrakis(tetrahydrofuran) complexes of aryl calcium iodides and bromides show the alkaline earth metals in an octahedral environment with the anionic ligands in a *trans* position. The Ca−C bond lengths depend on the coordination number of the calcium atom. In $[Ca(Mes)_2(thf)_3]$ with a five-coordinate calcium atom, Ca−C bond lengths of 252 pm are observed. In $[Ca(Aryl)X(thf)_4]$ with six-coordinate metal atoms, values of approximately 257 pm are found, whereas in $[Ca(dme)_2I(Ph)(thf)]$, a Ca−C distance of 262 pm is observed. All of these aryl calcium derivatives show very acute C-C-C bond angles at the *ipso* carbon atom. This is a consequence of the repulsion between the lone pair with the anionic charge and the neighboring C−C bonds.[43,44] This effect should increase with increasing ionic character of the heteropolar metal–carbon bonds.

Quantum Chemical Investigations

Structures and aggregation of organocalcium compounds: Unique structures of d^0-metal compounds fascinate many research groups.[50] Quantum chemical investigations also include organic compounds of the heavy alkaline earth metals. Solvent-free monomeric dimethylmagnesium and -calcium are predicted to be linear, whereas the strontium and barium derivatives should be bent at the alkaline earth metal.[51] Similar results have been obtained for the alkaline-earth-metal dihydrides.[52] Explanations for this finding include 1) d-orbital participation at the alkaline earth metals (which are isolelectronic with the three-valent scandium group and the four-valent titanium group elements), 2) reverse polarization of the soft metal atoms by the anions, 3) van der Waals attraction between the anions through an induced dipole moment, and 4) a strictly ionic model with an alkaline-earth-metal dication with a sp^3 hybridization of the closed shell with the orbitals directing to the corners of a tetrahedron and the anions lying above the tetrahedral planes.[53] In solvent-free $[Ca(C(SiMe_3)_3)_2]$[18] the bent C-Ca-C fragment can be explained by agostic interactions between the Lewis acidic alkaline-earth-metal atom and the electron density of the Si−C bonds. This explanation is supported by a six-fold disordering of the calcium atom in the direction of all six silicon atoms.

Many ionic compounds are insoluble in common organic solvents; however, the aryl calcium derivatives show an extremely high solubility in ethers such as THF. Quantum chemical calculations show that a dimerization or even tetramerization through η^6-coordination of the calcium atom to the neighboring molecule would be favored in comparison to phenyl groups bridging through the *ipso* carbon atom.[47] This coordination must be accompanied by loss of coordinated ether ligands and it can be deduced from ab initio calculations that the bond energy of THF and of the η^6-bound phenyl groups is of a similar order of magnitude. In Figure 5 the dimeric and tetrameric molecules of PhCaI are shown.

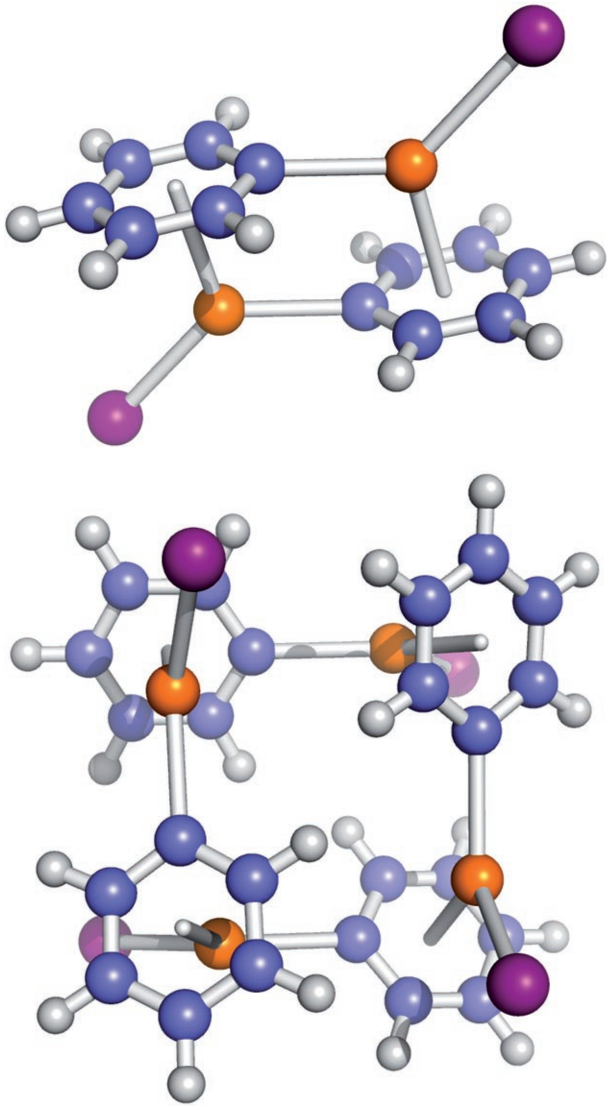


Figure 5. Representation of the molecular structures of dimeric (at the top) and tetrameric [CaIPh] (at the bottom) (color code: Ca orange, I violet, C blue, H grey) obtained from quantum chemical calculations (see the Supporting Information of reference [47] for details).

Diphenyldicalcium: Regarding the spectacular results in preparing organic metal(I) compounds of zinc[54,55] and cadmium[56] with metal–metal bonds, we are also interested in the question of whether calcium–calcium bonds in diaryldicalcium are stable. We should note that if aryl ligands are involved and closed-shell interactions may play a role, strong dispersion forces can be expected to be decisive for the structure of a potential calcium–calcium bond. Hence, standard methods of density functional theory (like BP86 or B3LYP), which can hardly describe this type of interaction, have to be accompanied by correlated ab initio calculations like MP2, CC2, or even the very computer-time-demanding CCSD(T) (see the Supporting Information of reference [47] for details and references on these calculations). In Figure 6, the reaction energetics at 0 K for the dimerization of two PhCa fragments is depicted. While BP86 and B3LYP favor

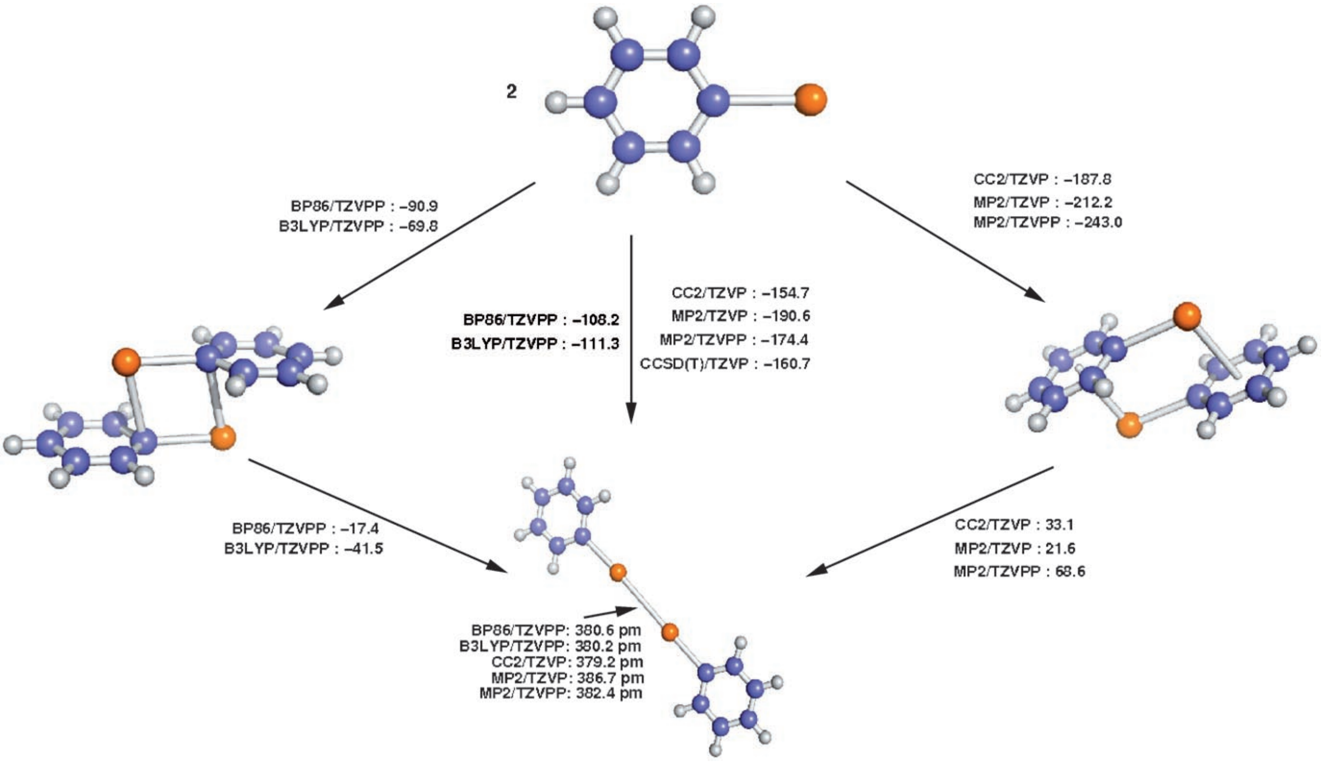


Figure 6. Representation of the reaction energetics at 0 K for the dimerization of two PhCa units. While BP86 and B3LYP favor the Ca–Ca bond, the ab initio methods MP2 and CC2 favor a more compact structure with η^6-coordination.

the Ca–Ca bond, the ab initio methods MP2 and CC2 calculations favor a more compact structure with η^6-coordination.

Having mentioned the dispersion problem of density functional methods, we may consider the MP2 and CC2 results as correct. However, the cyclic structure $[Ca(\mu\text{-}Ph)_2Ca]$ is less than 70 kJ mol^{-1} higher in energy relative to [PhCaCaPh]. The direct dimerization of PhCa to the bone-like linear structure [PhCaCaPh] results in a Ca–Ca bond energy between 154.7 kJ mol^{-1} (CC2) and 174.4 kJ mol^{-1} (MP2). A CCSD(T) single-point calculation on the CC2/RI/TZVP structure confirms these energies and yields 160.7 kJ mol^{-1}.[57] The BP86 and B3LYP bond energies are somewhat smaller so that we can consider density functional theory to yield lower values of interaction energies in case of molecules that are too large to be studied with ab initio methods. Natural bond orbital analyses indicate that the Ca–Ca bond can be qualitatively described by a dominating interaction of the 4s atomic orbitals of Ca with a minor p contribution. Coming to these larger [ArCaCaAr] derivatives we note that only for the case of the generic [PhCaCaPh] molecule did MP2/RI/TZVP and CC2/RI/TZVP structure optimizations show that a dimerization through a η^6-coordination should be the minimum structure (Figure 7), while phenyl substitution in *ortho* positions appears to stabilize the calcium–calcium bond (Figure 8, left).[57] These data indicate that nearly linear bis[2,6-diphenylphenyl calcium(I)] is the energetically most favored structure in the gas phase at 0 K. For this dimer, a Ca–Ca bond length of 378.3 pm and Ca–C distances of 248.0 pm are obtained with BP86/RI/TZVP.[57] A comparison of different quantum chemical methods (Figure 6) shows that the Ca–Ca bond length in [PhCaCaPh] is also about 380 pm, a result that hardly depends on the method chosen. The HOMO of the optimized linear structure of $[(2,6\text{-}Ph_2C_6H_3)Ca{-}Ca(C_6H_3\text{-}2,6\text{-}Ph_2)]$, represented in Figure 8, clearly shows large contribution to the electron density between the metal atoms. The disproportionation products $[Ca(C_6H_3\text{-}2,6\text{-}Ph_2)_2]$ and Ca are approximately 15 kJ mol^{-1} higher in energy than the Ca^I derivative, and the decomposition products $(2,6\text{-}Ph_2C_6H_3)_2$ and two Ca atoms are nearly 90 kJ mol^{-1} higher in energy (Scheme 7). Similar results were obtained for homologous bis[2,6-diphenylphenyl magnesium(I)] with a Mg–Mg bond dissociation energy of 175.4 kJ mol^{-1} and Mg–Mg and

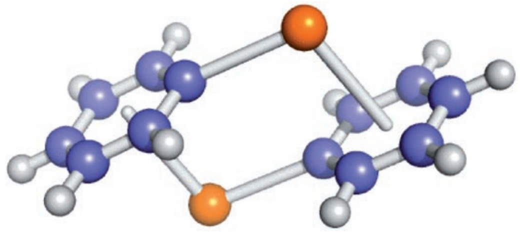


Figure 7. Molecular structure of dimeric phenyl calcium(I) (color code see Figure 4) obtained as the energetic minimum structure from quantum chemical calculations with MP2/RI/TZVP (see text).

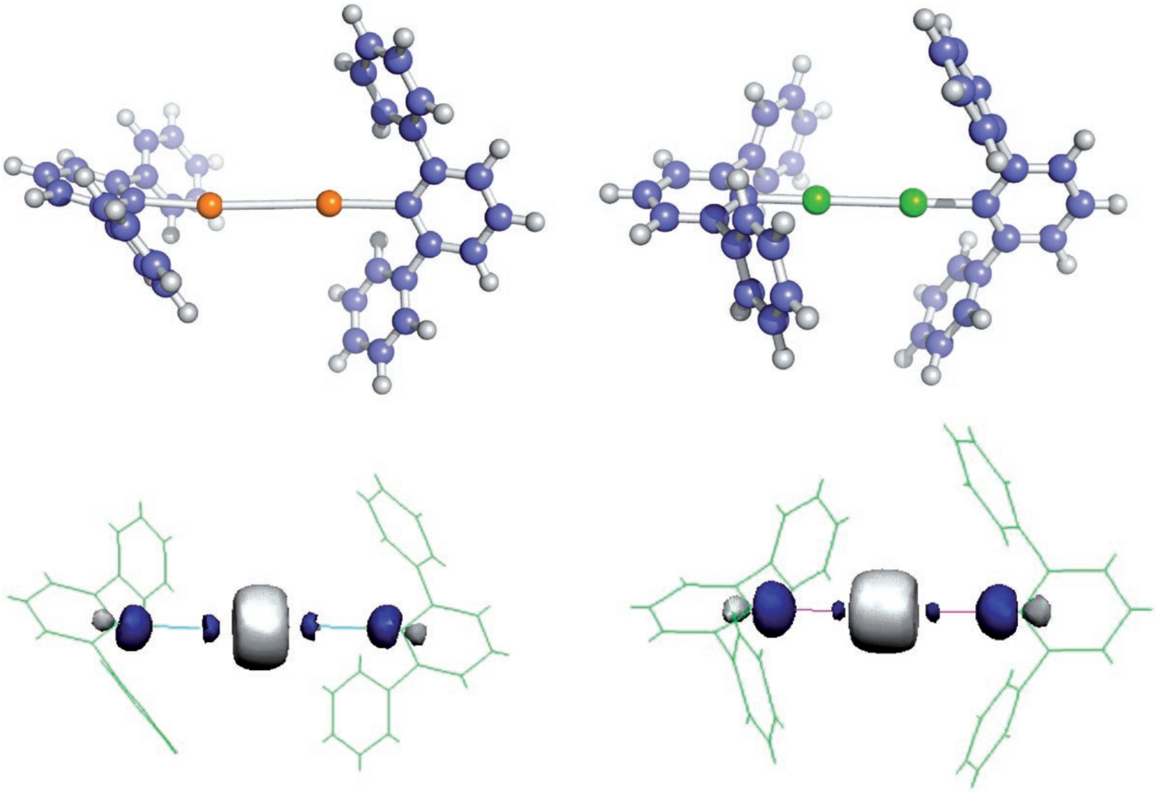
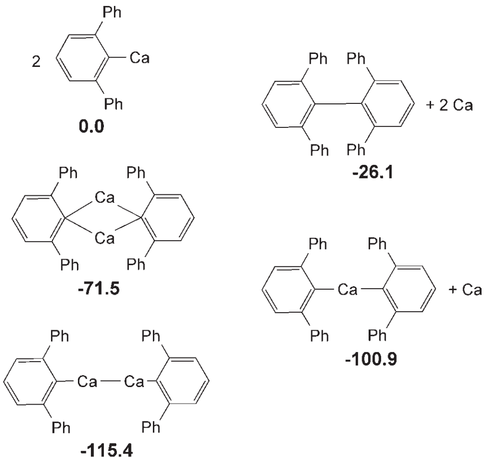


Figure 8. Representation of the molecular structure (at the top, color code see Figure 4, Mg light green) and of the HOMO (at the bottom) of bis[2,6-diphenylphenyl calcium(I)] (to the left) and bis[2,6-diphenylphenyl magnesium(I)] (to the right) obtained with BP86/RI/TZVP indicating a prominent contribution to the electron density between the alkaline-earth-metal atoms.



Scheme 7. Energy differences between [$Ca(2,6\text{-}Ph_2C_6H_3)$] (monomeric Ca^I compound), [$Ca_2(2,6\text{-}Ph_2C_6H_3)_2$] (Ca–Ca bond energy), [$Ca_2(\mu\text{-}C_6H_3\text{-}2,6\text{-}Ph_2)_2$], 2 Ca + $2,6\text{-}Ph_2C_6H_3\text{-}C_6H_3\text{-}2,6\text{-}Ph_2$ (decomposition), and Ca + [$Ca(2,6\text{-}Ph_2C_6H_3)_2$] (disproportionation) obtained with BP86/RI/TZVPP in $kJ\,mol^{-1}$ at 0 K.

Mg–C bond lengths of 283.8 and 213.4 pm, respectively (obtained with BP86/RI/TZVP). We should recall that these density functional theory results are likely to be a lower bound for the true bond energy, which is likely to be larger in view of our results for [PhCaCaPh].

These findings indicate that the *ortho* substituents stabilize diaryl dicalcium(I) not only for steric but also for electronic reasons. However, solvation and aggregation processes, which can easily open up reaction channels for dominating side reactions, were neglected in these quantum chemical investigations.

Reactivity Studies

Metathesis reactions: On the one hand direct synthesis are only possible in ether-type solvents, on the other hand ether cleavage reactions are the main degradation reactions. In order to stabilize organometallic compounds several concepts can be applied, such as 1) low reaction temperatures, 2) enhancement of the coordination number (e.g., substitution of three THF by two DME molecules), and 3) steric shielding by bulky groups. However, methyl and halogeno moieties in *ortho* positions of the phenyl substituent lead to side reactions,[38] as described earlier in this article. Therefore, the substitution of the iodide by a bulky group seems to be a feasible choice. Taking advantage of the insolubility of KI, the metathesis reaction of [$CaI(Ph)(thf)_4$] with $KN(SiMe_3)_2$ yields nearly quantitatively [$Ca\{N(SiMe_3)_2\}(Ph)$-

$(thf)_3]$ with a five-coordinate calcium atom.[44] The bulky bis(trimethylsilyl)amido group reduces the tendency of ether cleavage reactions. This general principle allowed the synthesis of various organocalcium compounds. From a similar metathesis reaction $[Ca(Ph)(PPh_2)(thf)_4]$ (Ca–P 303.1(2), Ca–C 252.9(5) pm) can be isolated (Figure 9). Homoleptic

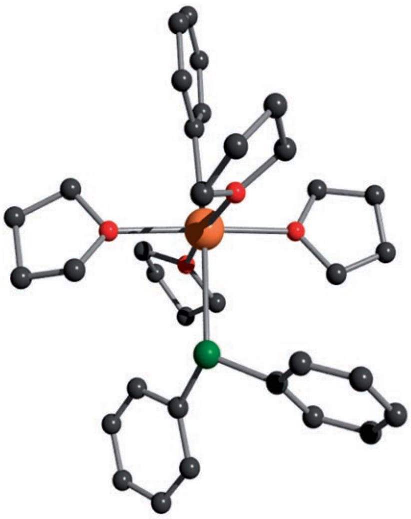
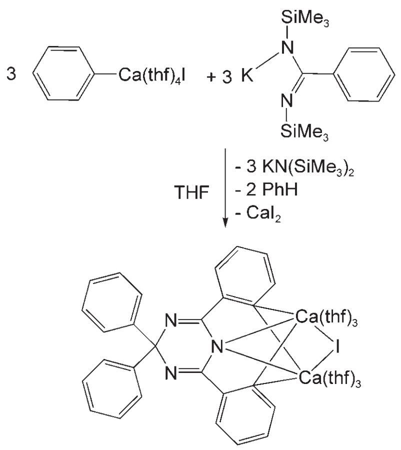


Figure 9. Molecular structure of $[Ca(Ph)PPh_2(thf)_4]$ (color code see Figure 1, P green). For clarity reasons, H atoms are not shown.

$[Ca(PPh_2)_2(thf)_4]$ (Ca–P 298.65(6) pm) can be obtained from the metathesis reaction of $[CaI_2(thf)_4]$ with two equivalents of $KPPh_2$. The molecular structure represented in Figure 10 shows a *trans* arrangement of the phosphanide substituents as observed earlier for $[Ca\{P(SiMe_3)_2\}_2(thf)_4]$ (Ca–P 291.1(2) and 292.4(2) pm).[58] However, other anions may shift the Schlenk equilibrium towards the homoleptic compounds. Thus, reactions of KO-C_6H_2-2,6-*t*Bu-4-Me and KCp with $[CaI(Ph)(thf)_4]$ yield the well-known complexes [Ca(O-C_6H_2-2,6-*t*Bu-4-Me$)_2(thf)_3]$[59] and $[CaCp_2(thf)_2]$,[60] respectively.

Figure 10. Molecular structure of $[Ca(PPh_2)_2(thf)_4]$ (color code see Figure 1, P green). Hydrogen atoms are omitted for clarity reasons.

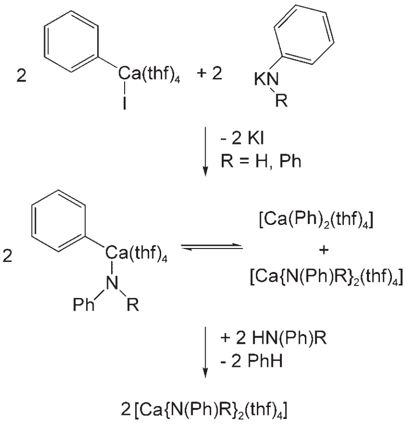
The reaction of $[CaI(Ph)(thf)_4]$ with potassium *N,N'*-bis(trimethylsilyl)benzamidinate according to Scheme 8 does not yield the expected metathesis product. Instead KN$(SiMe_3)_2$ is liberated and the remaining benzonitrile reacts with the calcium component: two phenyl groups are deprotonated in an *ortho* position and a dinuclear compound forms with a yield of approximately 20%.[44] The reaction of phenyl sodium with benzonitrile gives a similar reaction;[61] however, the deprotonation step seems to be characteristic for the calcium compounds and was not observed when PhNa was applied. This reaction was surprising because [Ca-$\{PhC(NSiMe_3)_2\}_2(thf)_2]$ is a stable compound which can be isolated.[62] In addition, it was shown that $KN(SiMe_3)_2$ reacts smoothly with $[CaI(Ph)(thf)_4]$ to yield $[Ca(Ph)\{N(SiMe_3)_2\}(thf)_3]$.[44] The product can be explained by assuming that the phenyl group reacts much faster than the bis(trimethylsilyl)amido ligand. If potassium *N,N'*-bis(trimethylsilyl)benzamidinate on the one side and $KN(SiMe_3)_2$ and PhC≡N on the other side are linked via an equilibrium and if benzonitrile is caught by the reaction shown in Scheme 8, all benzamidinate anions would be withdrawn from solution.



Scheme 8.

Metallation reactions: The metallation power of $[CaI(Ph)(thf)_4]$ can also be utilized in the reaction with 1,3-dimethoxybenzene. The direct synthesis of 2,6-$(MeO)_2C_6H_3I$ with calcium powder gives $[CaI\{2,6\text{-}(MeO)_2C_6H_3\}]$ with a rather poor yield of 56%,[38] and the metathesis reaction of CaI_2 with 2,6-$(MeO)_2C_6H_3K$ yields an oxygen-centered cage compound.[43] The *ortho*-directing methoxy groups lead to the deprotonation in an *ortho* position and an aryl-rich $[Ca_2I\{2,6\text{-}(MeO)_2C_6H_3\}_3(thf)_3]$ is isolated.[47] In this dinuclear complex the calcium atoms show coordination numbers of eight.

The synthesis of alkaline-earth-metal bis(amides) can easily be achieved for magnesium by employing dialkyl- or diarylmagnesium in deprotonation reactions of amines. The strontium and barium derivatives are accessible by deprotonation of the amine with the alkaline earth metals in liquid ammonia. However, calcium forms adducts with diphenylamine in liquid ammonia;[63] deprotonation was not observed. By using [CaI(Ph)(thf)$_4$] as starting material two pathways are possible, namely the deprotonation of Ph_2NH and the metathesis reaction with $KNPh_2$. The metathesis reaction of $KNPh_2$ with CaI_2 yielded [Ca(NPh$_2$)$_2$];[64] however, due to comparable solubility of KI and CaI_2 in ether solvents no clean reaction products can be obtained. Nevertheless, for a long time this was the only possibility to prepare [Ca(NPh$_2$)$_2$]. The most effective way to synthesize ether adducts of [Ca(NPh$_2$)$_2$] is a combination of the above proposed alternatives according to Scheme 9.[46] The amides of the heavy alkaline earth metals are only sparingly soluble, but are very sensitive towards moisture and air. The high reactivity and the nontoxicity of calcium suggest applications as an initiator for anionic polymerization processes; the homologous magnesium compound is already shown to be suitable in such fields of application.[65]



Scheme 9.

Despite the rather low solubility in common organic solvents, all alkaline-earth-metal bis(diphenylamides) crystallize as monomeric molecules. In contrast to this finding, the anilides of calcium, strontium, and barium precipitate as tetrameric [(thf)$_3$Ca{μ-N(H)Ph}$_3$Ca(thf){μ-N(H)Ph}]$_2$ and polymeric [Sr{μ-N(H)Ph}$_2$(thf)$_2$]$_\infty$ and [(thf)$_2$Ba{μ-N(H)Ph}$_2$(thf)Ba{μ-N(H)Ph}$_2$]$_\infty$. The one-dimensional polymer of the barium derivative with bridging nitrogen atoms is shown in Figure 11.[66] Coordinated THF as well as η^6-bound phenyl groups shield this chain structure.

Until very recently, the pK_a value of 25.8[67] for HN(SiMe$_3$)$_2$ was the limiting factor for the use as a metallating reagent, because only the alkaline-earth-metal bis[bis(trimethylsilyl)amides] were suitable synthons that were soluble in common organic solvents and available in good yields.[30] Therefore, past investigations were limited to substrates with very acidic hydrogen atoms. However, for the more reactive strontium and barium the activated metals often prove to be suitable metallation reagents. Thus barium reacts smoothly with secondary phosphanes, such as ethyl(phenyl)- and di(mesityl)phosphane, and yields nearly quantitatively polymeric [Ba{μ-P(Ph)Et}$_2$(thf)$_2$]$_\infty$ (Ba–P 324.8(1)–336.0(1) pm) with bridging phosphanide substituents and the molecular compound [Ba{P(Mes)$_2$}$_2$(thf)$_4$] (Ba–P 318.72(9) pm, Figure 12).[66] The larger bulkiness of the mesityl groups compared to trimethylsilyl substituents leads to smaller intramolecular distortions (Ba–P 315.8(6) and 319.0(6) pm) than were observed for [Ba{P(SiMe$_3$)$_2$}$_2$(thf)$_4$].[68]

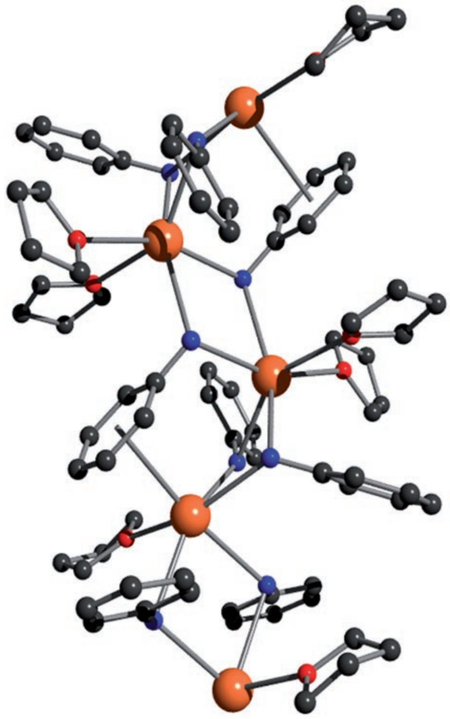


Figure 11. Part of polymeric [Ba{μ-N(H)Ph}$_2$(thf)$_2$]$_\infty$ (color code see Figure 1, N blue). Hydrogen atoms are omitted for clarity reasons. The nitrogen atoms bridge to Ba atoms which coordinate to either two THF molecules or one THF and a η^6-coordinated phenyl group.

Addition reactions: The transfer of aryl groups to other organometallic compounds leads to the formation of metallates. As an example, [CaI(Mes)(thf)$_4$] transferred the mesityl group to [V(Mes)$_3$] yielding [CaI(thf)$_5$]$^+$[V(Mes)$_4$]$^-$.[45] The transmetallation reaction (reaction of [V(Mes)$_3$] with calcium metal) also gave tetra(mesityl)vanadate anions shown in Figure 13, the counterion being [Ca(thf)$_6$]$^{2+}$. A third possibility to prepare tetra(mesityl)vanadates is the reduction of [V(Mes)$_4$] according to Scheme 10. However, the yield is rather poor. The vanadium(III) center of the tetra(mesityl)vanadate anion is in a distorted tetrahedral environment with two small (97.8°) and four large C-V-C bond angles (115.6°).

Transmetallation reactions: The difficulties and challenges during the preparation of organocalcium compounds

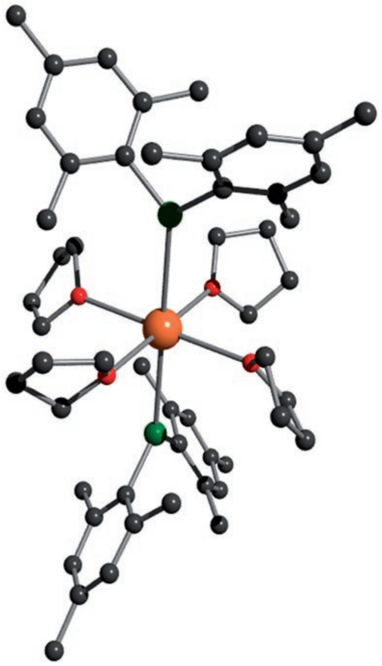


Figure 12. Molecular structure of $[Ba\{P(Mes)_2\}_2(thf)_4]$ (Mes: 2,4,6-trimethylphenyl, mesityl; color code see Figure 1, P green). For clarity reasons, H atoms are not shown.

prompted us to look for alternative procedures. The reaction of the heavy alkaline earth metals with $[Zn(CH_2SiMe_3)_2]$ yields the corresponding tris(trimethylsilylmethyl)zincates of calcium,[69] strontium, and barium.[70] However, decomposition into $[M(CH_2SiMe_3)_2]$ and $[Zn(CH_2SiMe_3)_2]$ was neither possible by changing the solvent nor by using high temperatures. Therefore, a more noble metal than zinc was chosen and phenyl copper was treated with activated calcium in THF according to Scheme 11. Extremely sparingly soluble $[(thf)_3Ca(\mu\text{-}Ph)_3Ca(thf)_3]^+[Ph\text{-}Cu\text{-}Ph]^-$ precipitated.[71] The six-coordinate calcium atoms are in octahedral environments with Ca–C bond lengths of 262.5(2), 261.3(2) and 260.5(3) pm; the planar diphenylcuprate anion displays characteristic Cu–C distances (191.0(3) pm). This is the second example of an organic cuprate of calcium in addition to the solvent-separated ion pair $[Ca(NH_3)_6]^{2+}[Cu(C{\equiv}CH)_3]^{2-}$ with Cu–C bond lengths of 203.1(7) pm and a nearly trigonal planar environment of the copper atom (C-Cu-C 119.89(4)°).[72]

The liberation of diphenylcalcium from this cuprate was not possible. Due to its insolubility in common organic solvents a further transmetallation and subsequent isolation of diphenyl calcium from this reaction failed as of yet.[71,73]

Prospects

In the last years the organocalcium chemistry has experienced a rapid development in many fields such as aryl,[17] alkynyl,[74] benzyl,[19–21] alkanediyl,[75] and triorganylsilyl calci-

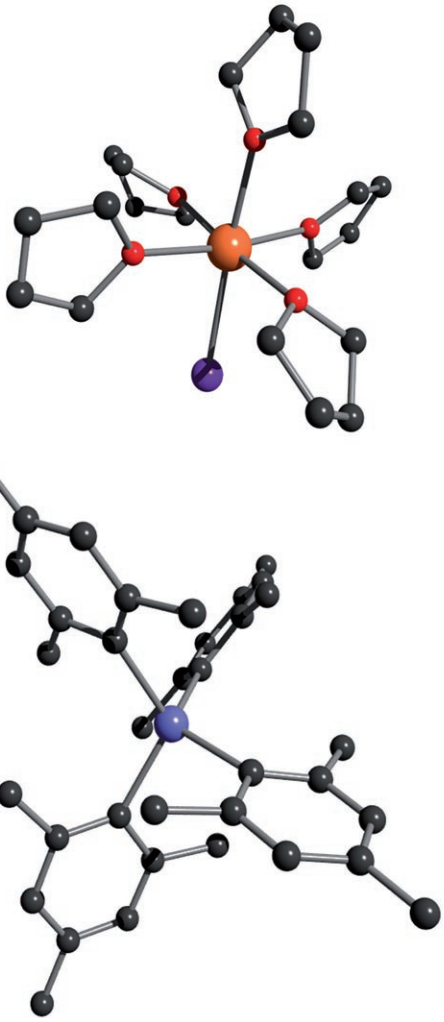
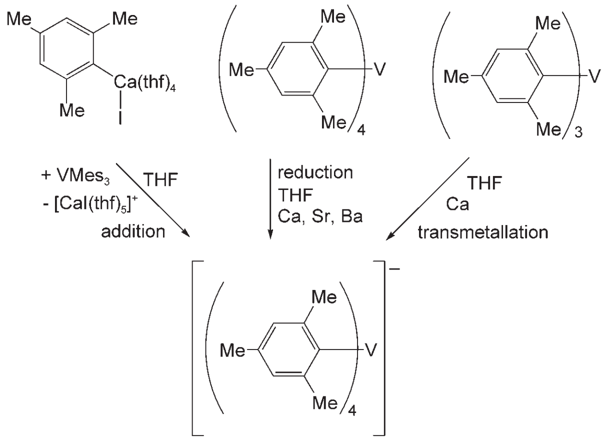
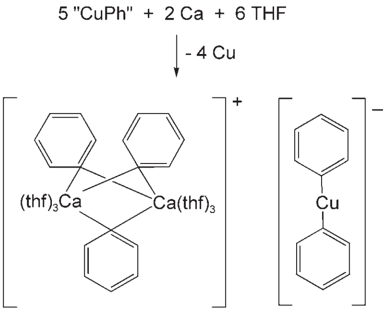


Figure 13. Molecular structure of the solvent-separated ion pair $[CaI(thf)_5]^+[V(Mes)_4]^-$ (color code see Figure 1, V light blue). The cation is shown at the top, the anion at the bottom. Hydrogen atoms are neglected for clarity reasons.



Scheme 10.



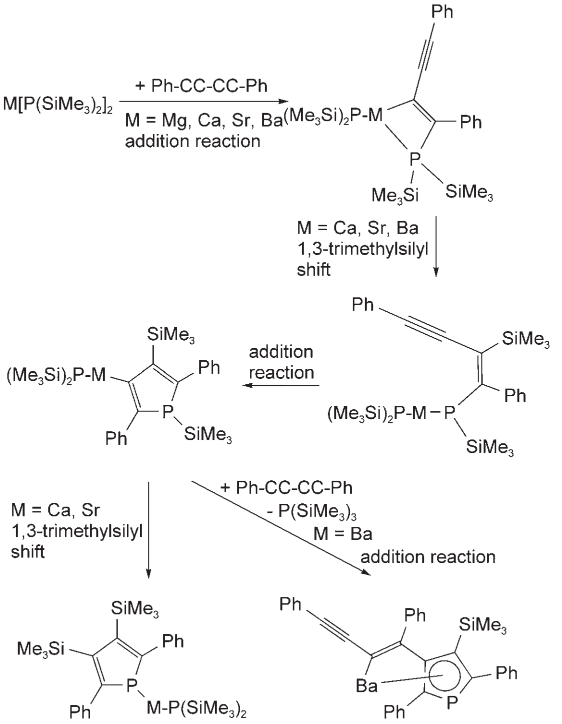
Scheme 11.

um compounds.[76] The majority of these compounds was prepared by means of metathesis reactions from potassium derivatives and now, the easy access of aryl calcium derivatives from the direct synthesis (Grignard reaction) might accelerate the development of the organic chemistry of the heavy alkaline earth metals. Due to the non-toxicity of calcium, many of these organocalcium compounds could serve as highly sought polymerization initiators for example, in ring opening polymerization of cyclic esters. Investigations towards this use were performed by many research groups[19,77,78] and are summarized in recent reviews.[79]

The low reactivity of the calcium metal towards 1,4-diiodobenzene yielded only the mono-insertion product [I-C_6H_4-CaI(thf)$_4$] even in the presence of excess of calcium powder, whereas diiodobenzene is able to react twice with magnesium shavings[41] or lithium reagents.[40] In contrast to the alkaline earth metal itself, 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 metallation, metathesis, and addition reactions. However, the higher reactivity of the organocalcium compounds compared to the lithium and magnesium derivatives also leads to a higher tendency to cleave ether. On the one hand, this fact enforces that reactions should be performed below room temperature; on the other hand, this reactivity can be utilized to obtain an enriched variety of products.

One example might illustrate the dependency of the reactivity from the alkaline earth metal. Due to the diagonal relationship in the periodic table, the CH and P^{III} moieties are often considered as isolobal fragments.[80] Therefore, the reactivity of [M{P(SiMe$_3$)$_2$}$_2$] (M = Mg, Ca, Sr, Ba) towards alkynes could serve as a representative example. The reaction is summarized in Scheme 12.

[Mg{P(SiMe$_3$)$_2$}$_2$] only shows the addition to one C≡C triple bond.[81] Employing the heavier homologous phosphanides, a 1,3-trimethylsilyl shift occurs followed by addition of the newly formed M–C bond to the other C≡C bond. For the calcium and strontium derivative again a 1,3-trimethylsilyl shift is observed[82] whereas for the barium derivative the insertion of another equivalent of 1,4-diphenylbutadiyne into the Ba–C bond is found.[81] Up to today, this organobarium compound is the only representative of an alkenyl complex of a heavy alkaline earth metal.



Scheme 12.

The fascination of the organomagnesium chemistry, which is still very vivid today, will be enriched and extended by the possibilities of the organometallic chemistry of the heavy homologous derivatives. Due to the existence of straight forward procedures for the synthesis of organic calcium compounds, the importance of this substance class will be enhanced and a wide range of applications will be developed.

Acknowledgements

We thank the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG, Bonn/Germany) and the Schweizer National Fonds (Proj. No. 200021–113479/1) for generous financial support of this research initiative. We also gratefully acknowledge the funding of the Fonds der Chemischen Industrie (Frankfurt/Main, Germany). We thank the Deutsches Museum, Bildstelle (Munich/Germany) for providing a picture of Victor Grignard (Figure 1). M.G. gratefully acknowledges the Ph.D. grant of the Fonds der Chemischen Industrie.

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