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Organocalcium Compounds

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Stabilization and Reactivity of the Lewis Acidic Solvated Phenylcalcium Cation**

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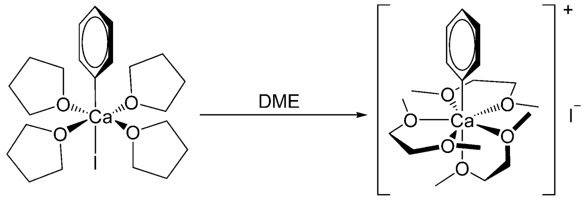
Calcium, the fifth most frequent element on earth, is the ideal metal for stoichiometric and catalytic applications owing to its non-toxicity, global abundance, and low cost. Furthermore, this alkaline-earth metal shows favorable chemical properties in its compounds, combining the beneficial behavior of the alkali metals (highly heteropolar bonds, high nucleophilicity of the counteranions) and Group 3 elements (d orbital participation, Lewis acidic character of the cation, catalytic activity[1]) as well as Group 13 metals (highly Lewis acidic nature).[2]

Like their magnesium counterparts,[3] arylcalcium halides are nowadays easily accessible by direct synthesis from calcium and the appropriate organyl halides. Redistribution of the anions converts these heteroleptic complexes RCaX into the homoleptic congeners CaR_2 and CaX_2, in agreement with the Schlenk equilibrium observed for magnesium.[4] However, this simple relationship given above falls short of the description of the diverse structures and compounds present in solution. It is well-known in organomagnesium chemistry that the addition of multidentate strong Lewis bases, such as crown ethers or cryptands[5] or even THF, can lead to solvent-separated ions, such as $[\{(thf)_3Mg\}_2(\mu\text{-}Cl)_3]_2^{2+}$-$[(Ph_2Mg)_2(\mu\text{-}Cl)_2]^{2-}$.[6] While homo- and heterobimetallic magnesiates are well-documented in organomagnesium chemistry and play key roles when it comes to the adjustment of reactivity and selectivity (the so-called turbo Grignard reagent),[7] organomagnesium cations are less common species. Only very few examples for mononuclear cationic alkylmagnesium reagents exist, such as $[(dme)_2(thf)MgMe]^+I^-$.[8] Other examples require non-coordinating anions, as in $[(L)Mg(n\text{Bu})]^+[BPh_4]^-$ [9] (L = 4,6-(MesN=$PPh_2)_2$dibenzofuran) or extremely weak and bulky Lewis bases, such as cyclopentadienide, fluorenide, and indenide, to stabilize the $[(14N4)MgMe]^+$ cation (14N4 = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane).[10] Mononuclear arylalkaline-earth metal cations are even more elusive species. $[(Cryptand)Mg(Tol)]^+[Mg(Tol)_3]^-$ (Tol = *para*-tolyl) was detected by NMR spectroscopy in solution after addition of a cryptand to $[Mg(Tol)_2]$ but it was not isolated.[11]

Only three mononuclear organocalcium cations have been characterized, which contain allyl,[12] cyclopentadienide,[13] and pentamethylcyclopentadienide anions,[14] respectively. In all of these compounds, the negative charge of the anion can be delocalized through the π-system of the ligand. Derivatives containing purely σ-bonded alkyl or aryl rests are unknown.

In earlier work,[15] it was established that Lewis base adducts of phenylcalcium iodide, such as $[(thf)_4Ca(Ph)I]$,[16] $[(thp)_4Ca(Ph)I]$,[15] $[([18]crown\text{-}6)Ca(Ph)I]$,[15] and $[(tmeda)_2Ca(Ph)I]$[17] (thp = tetrahydropyran, tmeda = *N,N,N′,N′*-tetramethylethylendiamine) adopt similar molecular structures as the corresponding calcium diiodide complexes, while for the related diarylcalcium compounds,[4] other variants on these structures were observed. Most of these calcium diiodide complexes crystallize as discrete neutral molecules; formation of separated ions is not observed in solid state. Exceptions were found for the 1,2-dimethoxyethane complex $[(dme)_3CaI]^+I^-$ [18] and the diethylene glycol dimethyl ether adduct $[(diglyme)_2CaI]^+I^-$.[19] However, earlier efforts to completely replace the THF ligands in $[(thf)_4Ca(Ph)I]$ by DME failed to yield a cationic phenylcalcium species, and $[(dme)_2(thf)Ca(Ph)I]$[16] was isolated instead. Therefore, our initial attempts focused on diglyme as solvent in ligand-exchange reactions starting from $[(thf)_4Ca(Ph)I]$. Unfortunately, no crystalline material was observed after removal of THF in vacuum und subsequent cooling. Therefore, ether exchange was repeated using 1,2-dimethoxyethane (Scheme 1), although this ligand is known to be easily degradable by strong bases.[20] To ensure complete removal of THF, the starting material was dissolved in DME, and thereafter the solvent was removed in vacuo. This procedure was repeated. The residue was recrystallized from DME,



Scheme 1. Formation of $[(dme)_3CaPh]^+I^-$ (**1**).

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yielding a pale orange solution from which colorless crystals deposited at −20 °C.

The single crystals consisted of approximately 95 % of $[(dme)_3CaPh]^+I^-$ (**1**) and 5 % of $[(dme)_3CaI]^+I^-$, with a superposition of the phenyl group and the calcium-bound iodide verifying again the similarity of calcium diiodide and phenylcalcium iodide complexes (Figure 1). Despite the large coordination number of seven, a short average Ca–C bond length of 251.7 pm was observed, which is due to a strong electrostatic attraction. In the related dinuclear $[(thf)_3Ca(\mu\text{-}Ph)_3Ca(thf)_3]^+$ cation with bridging phenyl groups, an average Ca–C bond length of 261.4(3) pm was reported.[21] The average Ca–I distance of 313 pm of superimposed $[(dme)_3CaI]^+I^-$ is also smaller than determined for $[(dme)_2(thf)Ca(Ph)I]$ (Ca–C 262.1 pm, Ca–I 319.2 pm[16]) with a seven-coordinate calcium center but in agreement with the data of pure $[(dme)_3CaI]^+I^-$ (Ca–I 312.0(3) pm).[18a]

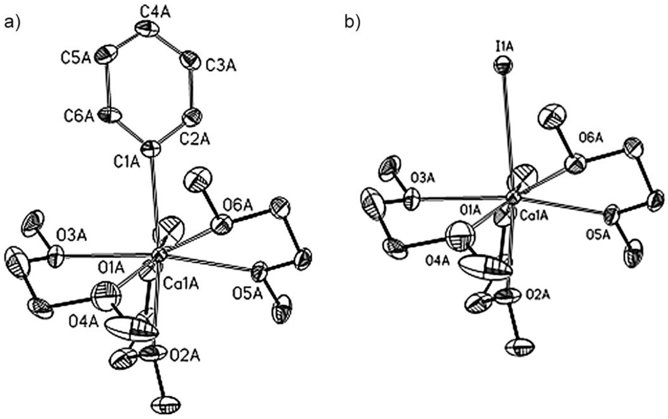


Figure 1. Molecular structures of the superimposed cations $[(dme)_3CaPh]^+$ (a) and $[(dme)_3CaI]^+$ (b). The asymmetric unit consists of two molecules A and B; only A is displayed. Ellipsoids are set at 40 % probability and H atoms are omitted for clarity. Selected bond lengths of molecule A [molecule B] [pm]: Ca1–C1 251.9(6) [251.5(6)], Ca1-I1 314.0(15) [312.3(11)], Ca1–O1 245.9(4) [243.3(3)], Ca1–O2 244.6(4) [244.0(3)], Ca1–O3 243.4(4) [247.1(3)], Ca1–O4 246.6(4) [245.2(3)], Ca1–O5 240.4(4) [246.1(4)], Ca1–O6 243.9(3) [242.3(4)]; angles (deg.): C2-C1-C6 112.5(5) [112.2(5)], Ca1-C1-C2 124.7(4) [120.7(4)], Ca1-C1-C6 121.5(4) [125.4(4)].[28]

As expected, narrow endocyclic C2-C1-C6 angles (av. 112.4°) were found for the $[(dme)_3CaPh]^+$ cation owing to electrostatic repulsion between the anionic charge in a sp^2 hybrid orbital at C1 and the neighboring C1–C2/6 bonds.

The solvent-separated species **1**, a heavier homologue of a Grignard reagent, is only sparingly soluble in hydrocarbons. Therefore, the NMR spectra were recorded in a solvent mixture of $[D_6]$benzene and DME. The *ipso*-carbon atom C1 exhibits a chemical shift of $\delta = 188.9$, which lies in the characteristic range for calcium-bound terminal phenyl groups.[16] During the measurements of the NMR spectra in a sealed NMR tube, DME degradation and the formation of methyl vinyl ether and benzene was observed (Figure 2 and Scheme 2). A similar finding has already been observed for the degradation of DME with *tert*-butyllithium.[22] Furthermore, a precipitate formed, formally consisting of ICa·OMe. Ether adducts of alkoxycalcium iodides were reported earlier with the calcium atoms in distorted octahedral environments and both anions embedded in the coordination sphere.[23] This intermediate methoxycalcium iodide complex can dismutate, forming the well-known species $[(dme)_3CaI]^+I^-$ and calcium methoxide. In presence of oxido-centered calcium species, a common impurity of the starting material $[(thf)_4Ca(Ph)I]$,[24] the cage compound $[\{(dme)Ca\}_4(CaI)_2(\mu_3\text{-}OMe)_8(\mu_6\text{-}O)]$ (**2**) was observed to a minor extent.

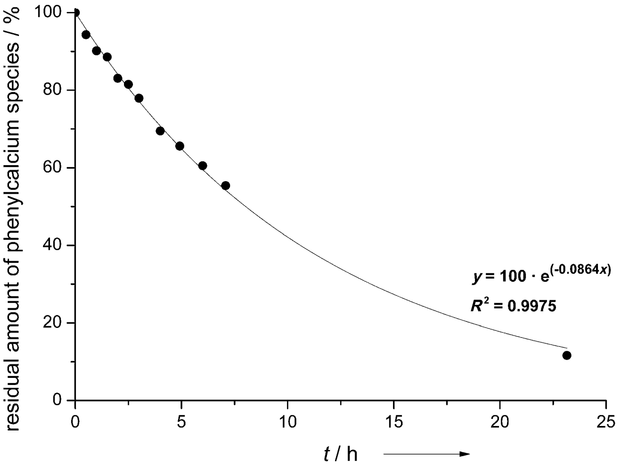
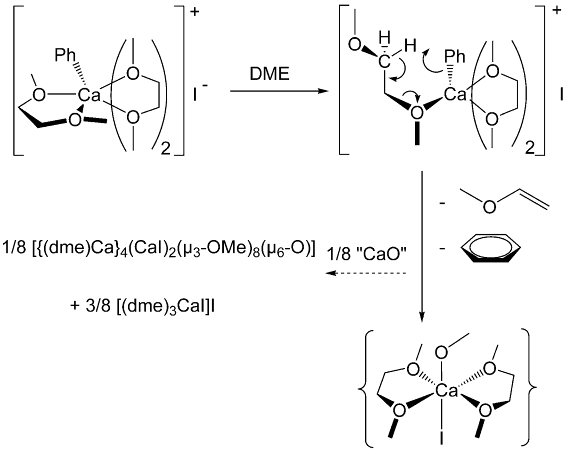


Figure 2. Decay of $[(dme)_3Ca(Ph)]^+I^-$ (starting concentration 0.05 M) in a solvent mixture of $[D_6]$benzene and 1,2-dimethoxyethane (DME/$[D_6]$benzene 3:1) at ambient temperature.



Scheme 2. Proposed mechanism for the decomposition of **1**.

A few crystals of hexanuclear species **2** were isolated from the degradation reaction of phenylcalcium iodide in a solvent mixture of toluene and DME (Figure 3). This cage compound consists of an oxygen-centered Ca_6 octahedron. All of the faces are capped by methoxy groups. Such oxide-centered Ca_6 octahedral cages seem to be one of the characteristic degradation products, and they were observed earlier for the decomposition by a heterobimetallic calcium/zinc system

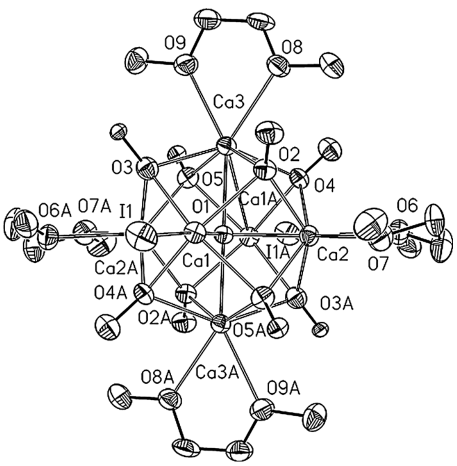


Figure 3. Molecular structure of **2**. Symmetry-equivalent atoms ($-x+0.5$, $-y+0.5$, $-z$) are marked with the letter "A". Ellipsoids are set at 40% probability and H atoms are omitted for clarity. Selected bond lengths [pm]: Ca1–I1 313.88(16), Ca1–O1 229.78(14), Ca1–O2 237.7(5), Ca1–O3 239.1(6), Ca1–O4A 235.7(5), Ca1–O5A 237.2(5), Ca2–O1 234.97(14), Ca2–O2 241.6(5), Ca2–O4 238.3(5), Ca2–O6 252.7(6), Ca2–O7 248.7(6), Ca2–O3A 243.0(5), Ca2–O5A 239.3(5), Ca3–O1 235.98(14), Ca3–O2 238.3(5), Ca3–O3 239.2(5), Ca3–O4 238.0(5), Ca3–O5 239.7(5), Ca3–O8 253.4(5), Ca3–O9 252.1(6); Ca1···Ca2 329.1(2), Ca1···Ca3 330.2(2), Ca2···Ca3 331.0(2), Ca1···Ca2A 328.2(2), Ca1···Ca3A 328.6(2), Ca2···Ca3A 335.0(2).[28]

in THF[25] or as side product of the decomposition of calcium phosphanides in DME.[26] The iodine atoms are bound to two opposite calcium atoms of the octahedron, whereas the other four alkaline-earth metal atoms complete their coordination spheres with DME ligands. Owing to electrostatic reasons, the Ca–O1 bonds to the inner oxide are significantly shorter than to the methoxy anions. As expected, the DME ligands show the largest Ca–O distances. The Ca1–I1 distance of 313.9(2) pm lies in the expected range.

Despite the fact that calcium compounds usually show very similar chemical and structural behavior to the corresponding ytterbium(II) complexes, strikingly different properties are observed for the DME derivatives. Recrystallization of "$(dme)_n$Yb(Ph)I" from a solvent mixture of DME and hexane yielded $[\{(dme)_4Yb^{II}\}\{(dme)Yb^{III}Ph_4\}_2]$, a quite unusual mixed-oxidation-state rare-earth metal–organic complex.[27] Stabilization of the very Lewis acidic $[(dme)_3Ca(Ph)]^+$ cation obviously requires the non-redox activity of the metal center.

In conclusion, the substitution of the THF ligands of $[(thf)_4Ca(Ph)I]$ by bidentate DME enforces dissociation of the Ca–I bond, and the formation of a solvent-separated arylcalcium cation is observed. This unique and highly reactive complex $[(dme)_3CaPh]^+I^-$ easily loses a DME ligand making the Lewis acidic metal center accessible to substrates. The high reactivity of the $[(dme)_3CaPh]^+$ cation leads to degradation of DME, yielding calcium methoxides and methyl vinyl ether. This calcium-based organometallic complex, $[(dme)_3CaPh]^+I^-$, can be handled in solution owing to the non-redox activity of the alkaline earth metal, and it extends the reactivity scale for calcium-based organometallics without the disadvantage of dealing with mixed-metal reagents.

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[28] CCDC 912073 ($[(\mathrm{diglyme})_2\mathrm{CaI}]^+\mathrm{I}^-$), CCDC 912074 ($[(\mathrm{dme})_3\mathrm{CaPh}]^+\mathrm{I}^-$, **1**), and CCDC 912075 ($[\{(\mathrm{dme})\mathrm{Ca}\}_4(\mathrm{CaI})_2(\mu_3\text{-}\mathrm{OMe})_8(\mu_6\text{-}\mathrm{O})]$, **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.