Heteroleptic Phenylcalcium Derivatives via Metathesis Reactions of $PhCa(thf)_4I$ with Potassium Compounds

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The metathesis reactions of $(thf)_4Ca(Ph)I$ with the corresponding potassium compounds KR yield the heteroleptic arylcalcium derivatives $(thf)_3Ca(Ph)[N(SiMe_3)_2]$ (**1**) and $(thf)_4Ca(Ph)PPh_2$ (**2**), due to the insolubility of KI in common organic solvents. However, the reaction of KCp and KOC_6H_2-2,6-*t*Bu-4-Me with $(thf)_4Ca(Ph)I$ give the homoleptic compounds $(thf)_2CaCp_2$ (**3**) and $(dme)CaCp_2$ (**4**) (depending on the solvent) as well as $(thf)_3Ca(OC_6H_2$-2,6-*t*Bu-4-$Me)_2$ (**5**). Diphenylcalcium decomposed under these reaction conditions. The reaction of $K[(Me_3SiN)_2CPh]$ with $(thf)_4Ca(Ph)I$ yields $[\{(thf)_3Ca\}_2\{4,4\text{-}Ph_2\text{-}2,6\text{-}(C_6H_4)_2C_3N_3\}(\mu\text{-}I)]$ (**6**). This dihydrotriazine derivative forms due to a slow liberation of benzonitrile from the starting *N*,*N*′-bis(trimethylsilyl)benzamidinate. A solvent change in order to shift the Schlenk equilibrium ($2\ PhCaI \rightleftharpoons CaPh_2 + CaI_2$) toward the homoleptic diphenylcalcium leads immediately to ether cleavage reactions and the formation of $[\{(Et_2O)CaPh_2\}_4\cdot(Et_2O)CaO]$ (**7**), which precipitates from diethyl ether. This cage compound contains an oxygen-centered Ca_5 square pyramid with the phenyl groups bridging all Ca···Ca edges.

Introduction

Arylcalcium halides are accessible via the direct synthesis of aryl iodide or bromide with activated calcium in THF at low temperatures.[1,2] These heavy Grignard reagents show extremely high reactivity, which leads to ether cleavage reactions. This decomposition yields the oxygen-centered cage $[(thf)_7Ca_4(\mu_4\text{-}O)(\mu\text{-}I)_3(\mu\text{-}Ph)_3]$ with a Ca_4 tetrahedron.[3] Therefore, these phenylcalcium halides have to be handled at low temperatures throughout the whole synthesis. This fact limits the field of application. In order to raise the thermal stability and to shield the reactive Ca−C bond, the substitution of the halide anion by bulky substituents seems to be a suitable concept. The bis(trimethylsilyl)amide ligand is known to stabilize small coordination numbers and mononuclear compounds and, in addition, is a good leaving group. Due to the shielding ability, the thermal stability as well as the solubility in common organic solvents usually is enhanced by this bulky group.

In general, there exist several procedures for synthesizing heteroleptic calcium compounds of the type $RCaN(SiMe_3)_2$. The metathesis reaction of $Cp^*_2Ca(thf)_2$ with $LiN(SiMe_3)_2$ yielded $Cp^*Ca(thf)_3N(SiMe_3)_2$ and $LiCp^*$.[4] Organylcalcium iodide reacted with $KN(SiMe_3)_2$ to form the heteroleptic calcium derivatives, whereupon KI precipitates.[5,6] An equimolar reaction of $Ca[N(SiMe_3)_2]_2$ with H-acidic substrates also gave the corresponding heteroleptic compounds.[7] The various application fields of these heteroleptic calcium organic compounds include derivatization with H-acidic substrates[8,9] as well as their use as catalysts in hydroamination reactions[10] and the ring-opening polymerization of lactides.[11,12]

Here, the metathesis reaction of $(thf)_4Ca(Ph)I$ with KR is investigated. The insolubility of KI in common organic solvents prevents the formation of heterobimetallic compounds. However, in some cases the dismutation reactions lead to the formation of homoleptic diphenylcalcium and CaI_2.

Results and Discussion

Phenylcalcium iodide was prepared by reacting activated calcium powder with iodobenzene at low temperatures.[2,3] This

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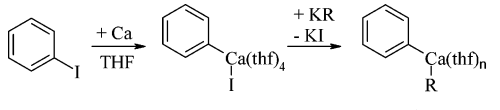
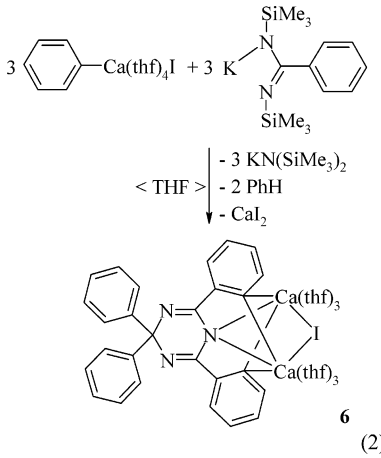
heavy Grignard compound has to be prepared in ether solution; no direct synthesis was observed in hydrocarbons. However, even above −30 °C ether cleavage reactions occurred. Therefore, $PhCa(thf)_4I$ was reacted at low temperatures with potassium bis(trimethylsilyl)amide according to eq 1, which yielded $PhCa(thf)_3N(SiMe_3)_2$ (**1**). This complex showed a half-life of 10 days in THF at room temperature. In order to prove the generality of the reaction, several substrates were employed such as potassium diphenylphosphanide and cyclopentadienide. Whereas the heteroleptic phenylcalcium diphenylphosphanide **2** was accessible by this procedure in high yields, the heteroleptic phenylcalcium cyclopentadienide underwent a dismutation into the well-known[13] homoleptic calcocene $(thf)_2CaCp_2$ (**3**); diphenylcalcium decomposed and was not observed under these reaction conditions. A solvent change to the bidentate 1,2-dimethoxyethane (DME) gave a similar reaction, and the well-known[14] $(dme)CaCp_2$ (**4**) was isolated. In addition, also potassium 2,6-di-*tert*-butyl-4-methylphenolate yielded the well-known homoleptic $(thf)_3Ca(OC_6H_2\text{-}2,6\text{-}t\text{Bu}_2\text{-}4\text{-Me})_2$ (**5**).[15]



1 (R = $N(SiMe_3)_2$, n = 3),
2 (R = PPh_2, n = 4)

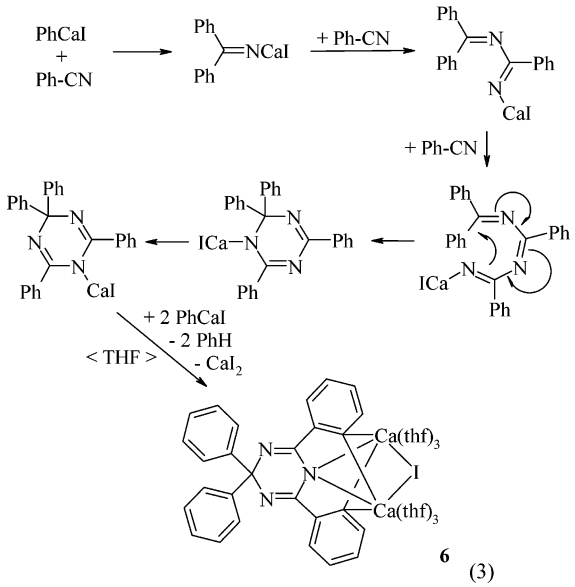
(1)

The addition of benzonitrile to a THF solution of **1** led to polymerization of the nitrile. In contrast to our expectation, no formation of *N*,*N*′-bis(trimethylsilyl)benzamidinate was observed, whereas $(thf)_2Ca[N(SiMe_3)_2]_2$ reacted smoothly with benzonitrile to give the corresponding bis(tetrahydrofuran)-calcium bis[*N*,*N*′-bis(trimethylsilyl)benzamidinate].[16] Therefore, potassium *N*,*N*′-bis(trimethylsilyl)benzamidinate was added to a THF solution of phenylcalcium iodide with the intention to isolate the metathesis product. However, the formation of [4,4-diphenyl-2,6-bis(1,2-phenylene)-1,3,5-triazacyclohexa-2,5-dien-1-yl]dicalcium iodide (**6**) was observed according to eq 2.



(2)

The key step is the slow liberation of benzonitrile from the *N*,*N*′-bis(trimethylsilyl)benzamidinate anion in order to prevent the polymerization of the nitrile. The mechanism can be explained similar to the reaction of phenylsodium with benzonitrile which was reported several decades ago.[17,18] In agreement with these reports, the first reaction step could be the addition of the $Ca-C_{Ph}$ bond to the nitrile function, yielding a diphenylimide as shown in eq 3, whereas a reaction of the



(3)

Ca−N bond with the nitrile function was not observed. Thereafter, two additional nitrile molecules could insert into the Ca−N bond. The ring closure would give a 1,2-dihydrotriazine derivative, which then rearranges via a 1,3-shift of the CaI unit into a 1,4-dihydrotriazine. The ortho CH moieties of the neighboring phenyl groups are activated, and a twofold deprotonation is observed by additional phenylcalcium iodide molecules with elimination of calcium diiodide.

Due to solubility problems, the metathesis reactions of $(thf)_4Ca(Ph)I$ with KR have to be performed at temperatures of approximately 0 °C. Low temperatures lead to extended reaction periods, due to the insolubility of the organopotassium compounds in common organic solvents. After the reaction of $(thf)_4Ca(Ph)I$ with potassium derivatives, heteroleptic arylcalcium compounds are obtained. However, even after a dismutation of these compounds we were not in the position to isolate diphenylcalcium. Therefore, diethyl ether was employed as the solvent in order to vary the Schlenk equilibrium and the relative solubilities of the involved species CaI_2, PhCaI, and $CaPh_2$. When the mixture was cooled, $(Et_2O)_4CaI_2$ crystallized, however, and diphenylcalcium was not obtained as a crystalline compound. Therefore, potassium bis(trimethylsilyl)amide was added at 0 °C to an Et_2O solution of phenylcalcium iodide freshly prepared from activated calcium and iodobenzene. KI precipitated and shifted the Schlenk equilibrium toward the homoleptic compounds $CaPh_2$ and $Ca[N(SiMe_3)_2]_2$. At these temperatures diphenylcalcium attacked ether and underwent ether cleavage reactions. This reactivity led to the formation of the oxygen-centered pentanuclear calcium cage $[\{(Et_2O)CaPh_2\}_4 \cdot (Et_2O)CaO]$ (**7**). The calcium atoms form a square pyramid, with all edges bridged by phenyl groups. A diethyl ether molecule is attached to each calcium corner of the polyhedron. Thus, the

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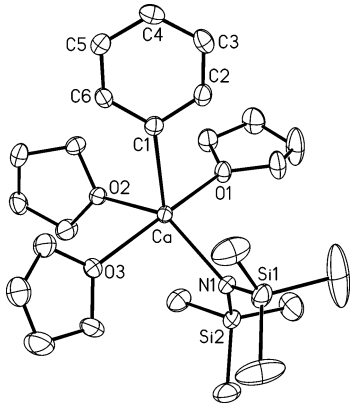

Figure 1. Presentation of the molecular structure of **1**. The ellipsoids are given at the 40% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles (deg): Ca−N1 = 234.7(2), Ca−C1 = 253.4(3), Ca−O1 = 239.2(2), Ca−O2 = 241.4(2), Ca−O3 = 241.0(2), N1−Si1 = 167.6(3), N1−Si2 = 168.5(3), C1−C2 = 140.9(4), C1−C6 = 140.7(4), C2−C3 = 138.2(5), C3−C4 = 137.7(5), C4−C5 = 138.8(4), C5−C6 = 138.2(4); C1−Ca−N1 = 128.7(1), C1−Ca−O1 = 90.70(9), C1−Ca−O2 = 96.84(8), C1−Ca−O3 = 98.18(9), Si1−N1−Si2 = 127.6(2), Ca−N1−Si1 = 118.7(1), Ca−N1−Si2 = 113.7(1), C2−C1−C6 = 112.1(3), Ca−C1−C2 = 118.9(2), Ca−C1−C6 = 129.0(2).

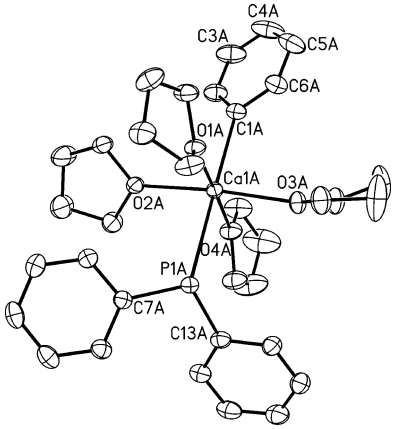

Figure 2. Molecular structure of **2**. The ellipsoids are given at the 40% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles (deg): Ca1A−P1A = 301.0(2), Ca1A−C1A = 253.4(5), Ca1A−O1A = 238.8(3), Ca1A−O2A = 236.9(3), Ca1A−O3A = 235.5(3), Ca1A−O4A = 238.9(3), P1A−C7A = 180.6(5), P1A−C13A = 180.8(5); P1A−Ca1A−C1A = 174.1(1), Ca1A−P1A−C7A = 116.8(2), Ca1A−P1A−C13A = 115.4(2), C7A−P1A−C13A = 107.9(2), Ca1A−C1A−C2A = 128.0(4), Ca1A−C1A−C6A = 118.8(4), C2A−C1A−C6A = 113.1(5).

apical Ca atom is in a distorted-octahedral environment, whereas the basal pentacoordinate alkaline-earth-metal atoms are in a distorted-trigonal-bipyramidal environment. In contrast to the ether cleavage of phenylcalcium iodide, which led to the formation of an iodine-containing cage molecule,[3] compound **7** crystallized halide-free from diethyl ether.

Molecular Structures. The bulkiness of the bis(trimethylsilyl)amido ligand led to a smaller coordination number of 5 for the alkaline-earth-metal center, whereas the diphenylphosphanide ligand is bound to a hexacoordinate calcium atom. The molecular structures and numbering schemes of **1** and **2** are represented in Figures 1 and 2. The asymmetric unit of **2** contains two crystallographically independent molecules which are very much alike, and therefore, this discussion is limited to molecule A. Both derivatives can be derived from the structure of the starting complex $PhCa(thf)_4I$. Whereas in **2** the iodide is substituted by a PPh_2 anion, in **1** the larger $N(SiMe_3)_2$ ligand replaces the iodide and one THF molecule. Due to this fact, a bent C−Ca−N fragment of 128.7(1)° and strongly different Ca−C1−C2/6 angles are observed. Due to the larger coordination number, the Ca−N bond lengths of 234.7(2) pm in **1** are greater than those observed for $L_2Ca[N(SiMe_3)_2]_2$ with L = THF (229.8(3) pm)[19] or L = $^1/_2$ DME (227.1(3) pm).[20] On the other hand, the Ca−C distance of 253.4(3) pm is smaller than in $PhCa(thf)_4Br$ (258.3(3) pm)[2] or in $PhCa(dme)_2(thf)I$ (262.1(5) pm)[2] with hexa- and heptacoordinate calcium atoms.

Trialkylsilyl-substituted phosphanides of calcium are well-known; however, only very few examples of alkyl- and aryl-substituted derivatives exist. Karsch and Reisky[21] prepared the bis(dimethylphosphanyl)(trimethylsilyl)methanide complex (average Ca−P = 304.3 pm). With bidentate (alkyl)(aryl)phosphanide ligands Ca−P bond lengths of 289.7(2)[22] and 296.6 pm (average value)[23] were observed. A similar average Ca−P value of 291.8 pm was found for $(thf)_4Ca[P(SiMe_3)_2]_2$.[24] In **2** a rather long Ca−P bond of 301.0(2) pm was determined. On the other hand, short Ca−C and Ca−O bonds of 253.4(5) pm and between 235.5(3) and 238.9(3) pm, respectively, were observed.

The small Ca−C distances lead to a distortion of the phenyl ring. The endocyclic C2−C1−C6 bond angles of **1** and **2** with values of 112.1(3) and 113.1(5)° are very small. Due to the high ionic character of **1** and **2**, these small angles can be explained by repulsive forces between the lone pair at C1 and the bonds C1−C2/C1−C6. This effect is enhanced by strong electrostatic attraction between the anionic C1 atom and the alkaline-earth-metal cation. For these reasons, the C1−C2/C1−C6 bond lengths to the ipso carbon atom are also slightly enhanced. The highly ionic character of the heavy Grignard compound **1** is supported by the amido ligand: the negative charge at the nitrogen atom is effectively back-donated to the silicon atoms, leading to short N−Si bonds and a large Si1−N1−Si2 angle.[25]

The THF adduct of phenylcalcium iodide is stable in THF and insoluble in hydrocarbons but dismutates in Et_2O via a Schlenk equilibrium. Diphenylcalcium which forms during the Schlenk equilibrium proved to be extremely thermally sensitive and very reactive with respect to ether cleavage reactions. The substitution of the iodide by the bulky bis(trimethylsilyl)amide group stabilizes the heteroleptic compound. No formation of homoleptic compounds was observed. Due to this fact, compound **1** is more stable and shows a half-life in THF at room temperature of approximately 10 days, which now will enable an establishment of an organocalcium chemistry. Remarkably, phenylcalcium amide **1** is soluble in hydrocarbons such as toluene, which is in contrast to the behavior of the heavy Grignard reagent $PhCa(thf)_4I$. This fact also expands the field of application. Also for **2** there was no Schlenk equilibrium

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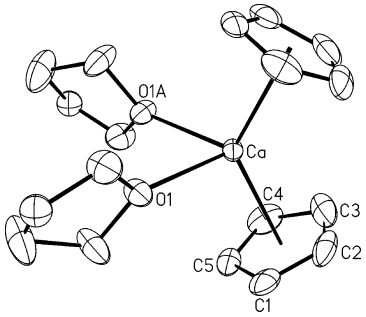

Figure 3. Molecular structure of **3**. The ellipsoids are given at the 40% probability level; hydrogen atoms are omitted for clarity. Symmetry-related atoms are marked with an A (A: $-x, y, -z + 0.5$). The parameters of (dme)$CaCp_2$ (**4**) are given in brackets. Selected bond lengths (pm) and angles (deg): Ca−O1 = 239.6(2) [241.8(2)], Ca−C1 = 270.0(3) [266.0(4)], Ca−C2 = 268.9(3) [266.3(5)], Ca−C3 = 268.2(3) [266.8(4)], Ca−C4 = 268.8(3) [266.5(4)], Ca−C5 = 269.4(2) [267.4(3)]; O1−Ca−O1A = 81.4(1) [68.3(1)].

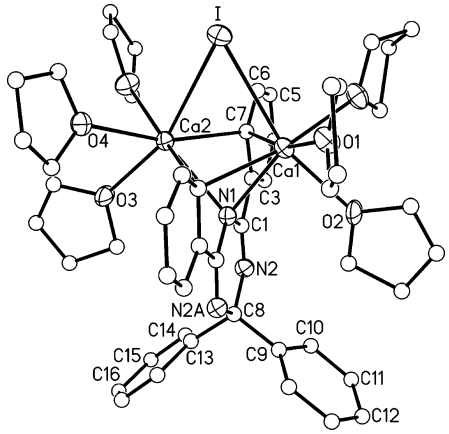

Figure 4. Molecular structure of **6**. The ellipsoids are given at the 40% probability level. The hydrogen atoms are omitted for clarity reasons, and the carbon atoms are drawn with arbitrary radii. Selected bond lengths (pm) and angles (deg): Ca1−I = 324.3(2), Ca2−I = 325.8(2), Ca1−N1 = 250.2(8), Ca2−N1 = 250.9(6), Ca1−C7 = 268.7(6), Ca2−C7 = 266.8(6), Ca1−O1 = 244.2(4), Ca1−O2 = 238.8(6), Ca2−O3 = 241.1(6), Ca2−O4 = 246.7(4), N1−C1 = 137.2(6), C1−N2 = 128.6(6), N2−C8 = 148.7(5), C1−C2 = 150.7(7), C8−C9 = 152(1), Ca1···Ca2 = 314.4(2); Ca1−I−Ca2 = 57.85(4), Ca1−N1−Ca2 = 77.7(2), Ca1−C7−Ca2 = 71.9(1).

operative and this derivative was even more stable than **1** in THF at room temperature, probably due to the higher coordination number of the calcium atom and hence a more effective shielding of the Ca−C bond. Whereas $PhCa(thf)_4I$ decomposes upon isolation, crystalline **1** and **2** can be stored at 0 °C for many weeks without decomposition.

The molecular structure of $(thf)_2CaCp_2$ (**3**) is represented in Figure 3. The cyclopentadienide anions are η^5-bound to the calcium atom. The alkaline-earth-metal atom is strongly distorted tetrahedrally surrounded by four ligands with a small O1−Ca−O1′ angle of 81.4(1)°. The Ca−O distance of 239.6(2) pm as well as the Ca−C bond lengths between 268.2(3) and 270.0(3) pm lie in the characteristic regions. The substitution of both of the THF ligands by a 1,2-dimethoxyethane molecule in **4** leads to a slight shortening of approximately 2 pm for the Ca−C bonds, whereas the Ca−O distances increase to 241.8(2) pm, due to a slightly enhanced ring strain (O−Ca−O′ = 68.3(2)°). Calcocenes represent a well-investigated substance class and have been summarized in several articles.[26]

The molecular structure of **6** is shown in Figure 4. The molecule contains a crystallographic mirror plane ($x, -y + 0.5, z$), and the symmetry-related atoms are marked with an "A". The seven-coordinate calcium atoms show a rather large average distance of 250.7 pm to the amido function of the dihydrotriazine moiety, due to the large coordination number and the bridging mode of this anion. For the same reason the Ca−C bond lengths are elongated as well. The Ca−I contact is only slightly larger than in arylcalcium iodides with six-coordinate metal centers and terminally bound halide anions. The reason is the enhanced electrostatic attraction between the soft and polarizable anion and two positively charged alkaline-earth-metal atoms with a very small Ca1−I−Ca2 bond angle of only 57.88(5)°.

The 2,6-bis(1,2-phenylene)-1,4-dihydrotriazine fragment is planar. Despite this orientation, the anionic charge is localized on the planar dihydrotriazine unit; the C1−C2 bond length of 150.6(9) pm shows that a delocalization into the phenylene moieties can be excluded. The double bond C1−N2 shows a value of 128.4(8) pm and is significantly shorter than the C1−N1 bond of 137.0(7) pm. The localization of the negative charge on N1 is a consequence of the proximity of two cations. The N2−C8 bond length is widened, due to the sp^3 hybridization of C8 and its distorted-tetrahedral environment. In 2,4,6-triphenyl-1,3,5-triazine C−N bond lengths of approximately 134 pm were found, and the C−C distances between the triazine unit and the phenyl groups were 148 pm.[26] The molecular structure of 2,2,4,6-tetraphenyl-2,3-dihydro-1,3,5-triazine showed that the lone pair of the amino nitrogen atom was included in a delocalized π-system and N−C bond lengths to the neighboring sp^2- and sp^3-hybridized carbon atoms showed values of 134.6(3) and 146.8(4) pm, respectively.[27] In compound **6** the delocalization is less pronounced than in this neutral hydrogenated molecule. In all of these molecules a delocalization between the triazine unit and the phenyl groups can be excluded on the basis of long C−C bonds, even though small tilt angles between the planes of the phenyl and triazine moieties were observed for 2,4,6-triphenyl-1,3,5-triazine.[28]

The pentanuclear complex $[\{(Et_2O)CaPh_2\}_4 \cdot (Et_2O)CaO]$ (**7**) is shown in Figure 5. The central oxygen atom O6 is in a square-pyramidal environment with Ca−O distances between 230.8(2) and 234.0(2) pm. The Ca(n)−O(n) distances (n = 1−4) to the diethyl ether ligands are approximately 10 pm longer, whereas the Ca5−O5 bond is even longer, due to the enhanced coordination number of 6 for Ca5. A similar finding is valid for the Ca−C distances. The pentacoordinate calcium atoms show Ca−C distances between 259.0(4) and 265.1(4) pm to the ipso carbon atoms of the phenyl groups. The Ca5−C(n) bond lengths vary between 267.0(4) and 273.4(4) pm.

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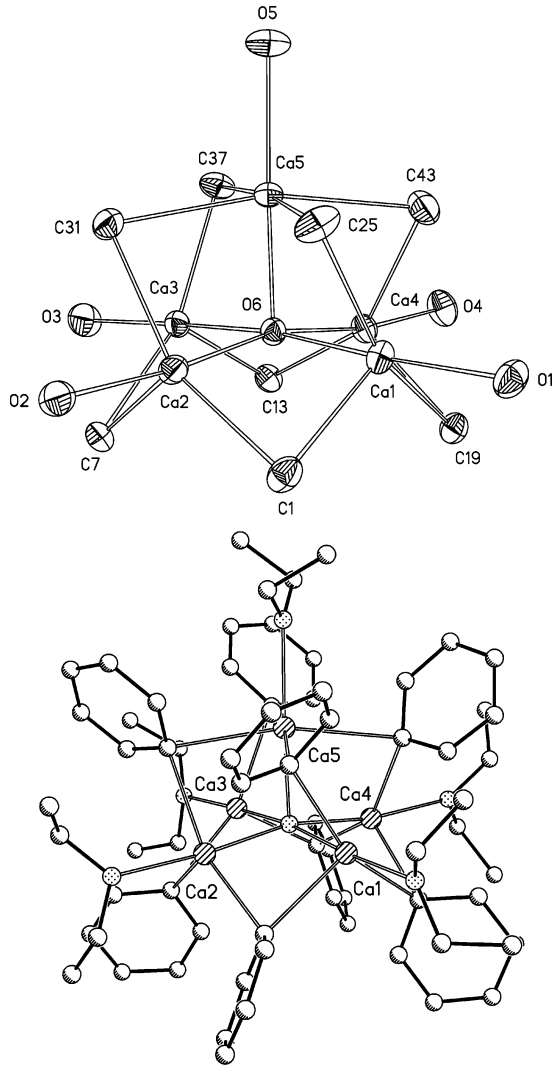

Figure 5. Molecular structure of **7**. The ellipsoids are given at the 40% probability level. The upper picture shows the inner core of the cage compound. The lower drawing depicts the whole molecule. All atoms are represented with arbitrary radii (C shaded, Ca hatched, O dotted), and the H atoms are omitted for clarity. Selected bond lengths (pm): Ca1−O1 = 242.9(3), Ca1−O6 = 234.0(2), Ca1−C1 = 261.4(4), Ca1−C19 = 261.9(4), Ca1−C25 = 265.1(4), Ca2−O2 = 243.6(3), Ca2−O6 = 232.1(2), Ca2−C1 = 262.2(4), Ca2−C7 = 259.0(4), Ca2−C31 = 263.4(4), Ca3−O3 = 243.6(3), Ca3−O6 = 232.8(2), Ca3−C7 = 262.0(4), Ca3−C13 = 261.6(4), Ca3−C37 = 264.4(4), Ca4−O4 = 242.0(3), Ca4−O6 = 230.8(2), Ca4−C13 = 259.9(4), Ca4−C19 = 259.0-(4) Ca4−C43 = 264.8(4), Ca5−O5 = 2501.(3), Ca5−O6 = 231.5-(2), Ca5−C25 = 267.1(4), Ca5−C31 = 272.7(4), Ca5−C37 = 267.0(4), Ca5−C43 = 273.4(4).

Summary and Perspective

In contrast to the long tradition of organoalkali-metal chemistry,[29] for many years little interest was devoted to the organometallic chemistry of the heavy-alkaline-earth metals. With the high-yield and large-scale synthesis of phenylcalcium iodide in addition to the systematic investigations on benzylcalcium,[30] alkylcalcium,[31] and alkynylcalcium derivatives,[32] the σ-bonded organometallic chemistry of the heavy-alkaline-earth metals is now in the process of leaving its infant stage, as calcocene chemistry did many years ago.[26] The Schlenk equilibrium can be influenced by the solvent and can be shifted via a metathesis reaction of PhCaI with potassium compounds. The insolubility of KI in THF and diethyl ether offers the possibility of substituting the iodine substituent by another anion. The bis(trimethylsilyl)amido and diphenylphosphanido ligands stabilize the heteroleptic arylcalcium compounds, whereas the cyclopentadienide and phenolate anions lead to a nearly quantitative dismutation of the arylcalcium compounds and the formation of the homoleptic derivatives. The substitution of the iodine atom by the bulky $(Me_3Si)_2N$ anion led to enhanced thermal stability, and the heavy Grignard reagent can be handled at 0 °C, whereas phenylcalcium iodide requires temperatures below −30 °C. Furthermore, the reaction with benzonitrile clearly showed the reactivity of this organometallic complex. Benzonitrile is polymerized by PhCaI in THF. However, if the benzonitrile concentration is very small, due to a slow liberation from the *N*,*N*′-bis(trimethylsilyl)benzamidinate anion, a trimer of benzonitrile with one added PhCaI moiety can be isolated. In addition, ortho metalation occurs and a dinuclear organocalcium complex is obtained. Diphenylcalcium is very reactive and cleaves ether, which finally yields the oxygen-centered pentanuclear cage compound $[\{(Et_2O)CaPh_2\}_4{\cdot}(Et_2O)CaO]$. Further investigations are in progress in order to evaluate the field of applications of the heavy Grignard reagents, especially in comparison to the widely explored organolithium and organomagnesium chemistry.

Experimental Section

All manipulations were carried out under an argon atmosphere under anaerobic conditions. The solvents were thoroughly dried and distilled under an argon atmosphere. $KPPh_2$[33] and $K[(Me_3SiN)_2NPh]$[34] were prepared according to literature procedures. All NMR spectra were recorded as $[D_8]$THF solutions. These compounds lose coordinated THF very easily once 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.

Synthesis of $PhCa(thf)_3N(SiMe_3)_2$ (1). To a cooled solution of 0.83 g of $KN(SiMe_3)_2$ (4.16 mmol) in 20 mL of THF was added dropwise 16.84 mL of a 0.247 M solution of $PhCa(thf)_4I$ in THF (4.16 mmol). A colorless precipitate formed immediately. After the mixture was stirred for an additional 1 h at 0 °C, all solids were removed and the volume of the filtrate was reduced to 9 mL. After addition of 10 mL of hexane and cooling to −90 °C, 1.45 g of colorless crystalline **1** (2.94 mmol, 71%) precipitated. ^{1}H NMR: δ −0.05 (s, 18H, $SiMe_3$), 1.73 and 3.59 (THF), 6.60−6.70 (m, 1H, *p*-H phenyl), 6.76 (t, 2H, $^3J_{H,H}$ = 6.8 Hz, *m*-H phenyl), 7.59 (d, 2H, $^3J_{H,H}$ = 6.2 Hz, *o*-H phenyl). $^{13}C\{^1H\}$ NMR: δ 5.81 ($SiMe_3$), 26.3 and 68.1 (THF), 122.7 (*p*-C phenyl), 125.4 (*m*-C phenyl), 140.8 (*o*-C phenyl), 189.3 (*i*-C phenyl).

Synthesis of $PhCa(thf)_4PPh_2$ (2). To 15.85 mL of a cooled 0.39 M red solution of $KPPh_2$ in THF (6.18 mmol) was added dropwise

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Table 1. Crystal Data and Refinement Details for the X-ray Structure Determinations of the Compounds 1−4, 6, and 7

	1	2	3	4	6	7
formula	$C_{24}H_{47}CaNO_3Si_2$	$C_{34}H_{47}CaO_4P\cdot{}^1/_2C_4H_8O$	$C_{18}H_{26}CaO_2$	$C_{14}H_{20}CaO_2$	$C_{51}H_{66}Ca_2IN_3O_6\cdot C_7H_8$	$C_{68}H_{90}Ca_5O_6$
formula wt	493.89	626.82	314.47	260.38	1116.26	1203.80
T/K	183(2)	183(2)	183(2)	183(2)	183(2)	183(2)
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic	orthorhombic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$Fdd2$ (No. 43)	$Pnma$ (No. 62)	$P\bar{1}$ (No. 2)
a/Å^3	17.6989(7)	11.1262(2)	13.4391(6)	13.5359(8)	26.112(5)	13.3626(4)
b/Å^3	10.7553(4)	12.4878(2)	9.6266(7)	22.6168(2)	15.678(3)	13.9814(3)
c/Å^3	17.5032(5)	27.3473(5)	14.2774(11)	9.1929(8)	15.041(3)	21.4210(6)
α/deg	90	87.823(1)	90	90	90.00	82.710(1)
β/deg	117.217(2)	88.844(1)	110.187(4)	90	90.00	75.234(1)
γ/deg	90	86.701(1)	90	90	90.00	64.449(1)
V/Å^3	2963.0(2)	3790.0(1)	1733.6(2)	2814.2(4)	6158(2)	3490.7(2)
Z	4	4	4	8	4	2
ρ/g cm^{-3}	1.107	1.099	1.205	1.229	1.204	1.145
μ/mm^{-1}	0.315	0.242	0.364	0.435	0.733	0.429
F(000)	1080	1352	680	1120	2336	1292
2*θ* range/deg	$4.6 < 2\theta < 55.0$	$3.4 < 2\theta < 55.0$	$5.2 < 2\theta < 55.0$	$7.6 < 2\theta < 55.0$	$4.0 < 2\theta < 55.0$	$4.4 < 2\theta < 55.0$
no. of indep rflns	6774	16 518	1990	1465	6878	15 827
no. of restraints	0	0	0	1	0	0
no. of params	280	761	95	79	329	710
wR2 (all data)[a]	0.1906	0.3188	0.1484	0.1246	0.2319	0.2321
R1 (all data)[a]	0.1174	0.1361	0.0717	0.0502	0.1201	0.1194
R1 ($I > 2\sigma(I)$)	0.0649	0.0977	0.0538	0.0461	0.0844	0.0736
s[b]	1.024	1.044	1.029	1.061	1.014	1.011
max/min resid density/e Å^{-3}	0.458/−0.460	1.155/−0.553	0.569/−0.337	0.986/−0.275	1.174/−1.232	0.889/−0.567
CCDC no.	614668	614669	614670	614671	626352	626353

[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] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

a solution of PhCa(thf)$_4$I in THF (0.247 M, 25.0 mL, 6.18 mmol). The solution turned orange, and a colorless powder precipitated (KI). After reduction of the volume to a fourth of the original volume and cooling to −90 °C, 3.07 g of colorless **2** (5.19 mmol, 84%) precipitated within 3 days. This compound can be recrystallized from THF and is stable at 0 °C. However, the crystals weather easily due to loss of intercalated THF. ^{1}H NMR: *δ* 1.73 and 3.49 (THF), 6.53 (t, 2H, *p*-H PPh$_2$), 6.78 (dt, 4H, $^4J_{H,H} = 0.6$ Hz, $^3J_{H,H} = 7.5$ Hz, *m*-H PPh$_2$), 6.75−6.90 (m, 3H, *p*-H + 2 × *m*-H phenyl), 7.34 (dt, 4H, $^4J_{H,H} = 1.4$ Hz, $^3J_{H,H} = 7.3$ Hz, *o*-H PPh$_2$), 7.60−7.75 (m, 2H, *o*-H phenyl). ^{13}C{^{1}H} NMR: *δ* 26.3 and 68.2 (THF), 120.5 (*p*-C PPh$_2$), 123.2 (*p*-C phenyl), 125.7 (*m*-C phenyl), 127.5 ($^3J_{C,P} = 5.7$ Hz, *m*-C PPh$_2$), 131.2 ($^2J_{C,P} = 16.4$ Hz, *o*-C PPh$_2$), 141.6 (*o*-C phenyl), 153.9 ($^1J_{C,P} = 36.0$ Hz, *i*-C PPh$_2$), 190.1 ($^2J_{C,P} = 8.0$ Hz, *i*-C phenyl). ^{31}P{^{1}H} NMR: *δ* −13.9 (s, PPh$_2$).

Synthesis of (thf)$_2$CaCp$_2$ (3) and (dme)CaCp$_2$ (4). A solution of potassium cyclopentadienide in DME (1.26 mol L^{-1}, 7.05 mL, 8.88 mmol) was added dropwise at 0 °C to a solution of (thf)$_4$Ca(Ph)I in DME (0.22 mol L^{-1}, 40 mL, 8.88 mmol). After complete addition a colorless precipitate formed. All solid materials were removed. These solids contained potassium and calcium. Extraction with three 20 mL portions of THF left a calcium-free solid. Reduction of the volume, addition of 10 mL of diethyl ether, and storage at −40 °C yielded 0.12 g of colorless crystals of Cp$_2$Ca(thf)$_2$ (**3**; 0.38 mmol, 9%).

The volume of the DME filtrate was reduced to half of the original volume and stored overnight at −25 °C. Colorless crystals of (dme)CaCp$_2$ (**4**; 0.66 g, 2.53 mmol, 57%). The NMR parameters of **3** and **4** are identical with published data.[13,14]

Synthesis of (thf)$_3$Ca(OC$_6$H$_3$-2,6-*t*Bu$_2$-4-Me)$_2$ (5). A solution of potassium 2,6-di-*tert*-butyl-4-methylphenolate in THF (0.13 mol L^{-1}, 40.0 mL, 5.2 mmol) was added dropwise at 0 °C to a solution of (thf)$_4$Ca(Ph)I THF (0.21 mol L^{-1}, 24.8 mL, 5.2 mmol). The solution turned cloudy immediately due to KI formation. All solids were removed. The solvent was distilled off the filtrate. The residue was dissolved in 20 mL of diethyl ether. This solution was cooled to −90 °C. Overnight 1.36 g of colorless crystals of **5** (2.05 mmol, 79%) precipitated. The NMR data are identical with the literature values.[15]

Synthesis of [{(thf)$_3$Ca}$_2${4,4-Ph$_2$-2,6-(C$_6$H$_4$)$_2$C$_3$N$_3$}(*μ*-I)] (6). A solution of phenylcalcium iodide in THF (0.298 mol L^{-1}, 11.42 mL, 3.40 mmol) was added dropwise at 0 °C to a suspension of potassium *N*,*N*′-bis(trimethylsilyl)benzamidinate (1.03 g, 3.40 mmol) in 10 mL of THF. In order to dissolve the potassium salt, the reaction mixture was warmed to room temperature and treated with ultrasound. During stirring of the solution at room temperature for 2 h, colorless KI precipitated. After removal of all solid material the filtrate was cooled to −90 °C. The first batch of crystals proved to be (thf)$_4$CaI$_2$. After removal of this calcium diiodide the volume of the mother liquor was reduced to half of the original volume. Thereafter, storage of this solution at −90 °C afforded the crystallization of 230 mg of colorless [{(thf)$_3$Ca}$_2${4,4-Ph$_2$-2,6-(C$_6$H$_4$)$_2$C$_3$N$_3$}(*μ*-I)] (yield: 0.22 mmol, 20%). ^{1}H NMR: *δ* 6.84 (dt, 2H, $^4J_{H,H} = 1.3$ Hz, $^3J_{H,H} = 7.2$ Hz), 6.9−7.2 (m, 8H), 7.55 (dd, 1H, $^4J_{H,H} = 1.4$ Hz, $^3J_{H,H} = 7.4$ Hz), 7.8−8.0 (m, 2H), 8.11 (dd, 2H, $^4J_{H,H} = 1.2$ Hz, $^3J_{H,H} = 8.4$ Hz), 8.22 (dd, 1H, $^4J_{H,H} = 1.6$ Hz, $^3J_{H,H} = 6.0$ Hz), 8.42 (dd, 1H, $^4J_{H,H} = 1.4$ Hz, $^3J_{H,H} = 6.4$ Hz), 8.77 (dd, 1H, $^4J_{H,H} = 1.8$ Hz, $^3J_{H,H} = 6.2$ Hz). ^{13}C{^{1}H} NMR: *δ* 124.4, 124.9, 125.9, 126.1 (4 × 2C, C4, C5, C6, C12), 127.4 (4C, C10 or C11), 127.7 (4C, C11 or C10), 133.3 (2C, C9), 144.0 (2C, C3), 151.3 (2C, C1 or C7), 157.1 (2C, C7 or C1), 164.5 (1C, C8), 190.7 (1C, C2).

Synthesis of [{(Et$_2$O)CaPh$_2$}$_4$·(Et$_2$O)CaO] (7). (a) Synthesis of Ether Solution of PhCaI. Activated calcium (1.02 g, 25.5 mmol) and 50 g of glass balls (i.d. 5 mm) were placed in a flask with 40 mL of diethyl ether. At 0 °C 3.63 g of iodobenzene (17.8 mmol, 0.7 of the stoichiometric amount) was added dropwise. This reaction mixture was stirred at 0 °C for 1 h and for an additional 4 h at room temperature. During this time a reddish brown suspension formed. All solid material was removed, and subsequent titration of an aliquot showed a yield of 82%.

(b) Reaction of PhCaI with KN(SiMe$_3$)$_2$. A solution of 2.70 g of potassium bis(trimethylsilyl)amide (13.5 mmol) in 10 mL of diethyl ether was cooled to 0 °C, and 36 mL of a 0.376 M solution

of phenylcalcium iodide in diethyl ether (36.0 mL, 13.5 mmol) was added dropwise. A colorless precipitate formed immediately, which was removed after 1 h and identified as KI. The volume of the filtrate was reduced to half of the original volume. At −90 °C 390 mg of colorless rhombic crystals of **7** precipitated. After reduction of the volume of the mother liquor and storage at −90 °C another crop of crystals (250 mg) was collected, which led to a total yield of 0.64 g (0.53 mmol, 32%). ^{1}H NMR: δ 6.70 (dt, 1H, $^4J_{H,H} = 1.6$ Hz, $^3J_{H,H} = 5.6$ Hz, *p*-H phenyl), 6.80 (t, 2H, $^3J_{H,H} = 7.2$ Hz, 2 × *m*-H phenyl), 7.63 (dd, 2H, $^4J_{H,H} = 1.6$ Hz, $^3J_{H,H} = 6.0$ Hz, 2 × *o*-H phenyl). ^{13}C{^{1}H} NMR: δ 122.8 (1C, *p*-C phenyl), 125.4 (2C, 2 × *m*-C phenyl), 140.8 (2C, 2 × *o*-C phenyl), 189.3 (1C, *i*-C phenyl).

X-ray Structure Determination of 1−4, 6, and 7.[35] Intensity data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz−polarization and for absorption effects.[36−38] Crystallographic data as well as structure solution and refinement details are summarized in Table 1.

The structures were solved by direct methods (SHELXS[39]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[40]). Compound **2** crystallized with two crystallographically independent molecules A and B; only molecule A is represented in Figure 2. Furthermore, two additional THF molecules are located between the calcium complexes. The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms except for the solvent molecules were refined anisotropically.[40] XP (SIEMENS Analytical X-ray Instruments, Inc.) and POVRAY were used for structure representations.

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Supporting Information Available: CIF files giving data collection and refinement procedures as well as positional coordinates of all atoms. 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 (CCDC-614668 (**1**), CCDC-614669 (**2**), CCDC-614670 (**3**), CCDC-614671 (**4**), CCDC-626352 (**6**), and CCDC-626353 (**7**)) contain the 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; e-mail deposit@ccdc.cam.ac.uk).

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(35) CCDC-614668 (**1**), CCDC-614669 (**2**), CCDC-614670 (**3**), CCDC-614671 (**4**), CCDC-626352 (**6**), and CCDC-626353 (**7**) contain the 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; e-mail deposit@ccdc.cam.ac.uk).

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