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Synthesis and Structure of an Arylcalcium Compound with an Unusual Calcium Tetrahedron Containing an Encapsulated Oxide

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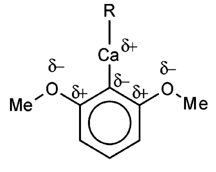
Summary: The attempted synthesis of homoleptic bis(2,6-dimethoxyphenyl)calcium reproducibly yielded a crystalline product of composition Ar_6Ca_4O, in which the Ca^{2+} ions span a tetrahedron, the six aryl ligands bridge the vertices, and O^{2-} occupies the center.

Although our understanding of heavier alkaline-earth-metal compounds (Ca, Sr, and Ba) with strong nucleophilic σ-bonded carbanions is growing steadily,[1,2] there is a lack of information on their aryl complexes. This is surprising, since the first calcium “Grignard analogues”, EtCaI and PhCaI, have been reported exactly a century ago by Beckmann.[3] Although Gilman could not reproduce Beckmann’s EtCaI,[4] the compound PhCaI could be prepared in at least some quantity; however, the product was never isolated and characterized. Later reports describe the synthesis of PhCaI by a variety of methods, but products and yields have only been determined indirectly by quenching reactions.[5−8] In addition, diphenylcalcium, prepared via reduction of Ph_2Hg, has been described, but no NMR data or structural data have been reported.[9]

It is likely that the isolation of pure well-defined arylcalcium compounds in reasonable yields is plagued by ether cleavage reactions, for which evidence has been reported.[10] Therefore, we focused on the syntheses of dipole-stabilized (2,6-dimethoxyphenyl)calcium complexes (**1**). Previous research on (2-methoxyphenyl)lithium and (2,6-dimethoxyphenyl)lithium complexes showed that the reactivity of aryllithium compounds can be effectively tamed to a level that enables even isolation of reaction intermediates (e.g. metastable ArLi−epoxide complexes could be crystallized).[11]



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In our synthetic approach toward defined arylcalcium complexes we want to avoid the use of arylmercury compounds but, instead, focus on a method that has been proven very successful in the preparation of reactive dibenzylcalcium complexes: the metathesis reaction between organopotassium compounds and CaI_2.[2d,e,g−i] (2,6-Dimethoxyphenyl)potassium was obtained by reaction of the easily accessible (2,6-dimethoxyphenyl)lithium[12] with $KOC(Me)(Et)_2$. A suspension of (2,6-dimethoxyphenyl)potassium and CaI_2 in THF was stirred over a period of 3 days.[13] After removal of THF, extraction of the product with benzene, and finally removal of the solvent a crude product in reasonable yield (ca. 90%) was obtained. Crystallization by slow diffusion of hexane in a benzene solution gave after 4 days a large crop of uniform colorless crystalline needles.

Crystal structure determination reveals an asymmetric unit containing a cluster (Figure 1) of the formal composition $[2,6\text{-}(MeO)_2C_6H_3]_6Ca_4O$, which could also be described by $[(2,6\text{-}(MeO)_2C_6H_3)_2Ca]_3\cdot[CaO]$. There is evidence that this oxidized product, which was obtained in 67% yield, is representative for the crystalline bulk product: (i) unit cell constants of several crystals from the same batch were similar, and (ii) reproducible elemental analyses of the crystalline bulk product show the correct composition.[13] The syntheses as well as the analyses of products obtained (X-ray and C,H analyses) could be reproduced.

The cluster contains a Ca_4O unit in which four Ca^{2+} ions span a tetrahedron around the central O^{2-} ion. The

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(2) Crystal structures of homometallic complexes with the following σ-bonded carbanions have been published. (a) $(Me_3Si)_2CH^-$: Cloke, F. G.; Hitchcock, P.; Lappert, M.; Lawless, G.; Royo, B. *J. Chem. Soc., Chem. Commun.* **1991**, 724. (b) $(Me_3Si)_3C^-$: Eaborn, C.; Hawkes, S.; Hitchcock, P.; Smith, J. D. *Chem. Commun.* **1997**, 1961. (c) $Ph_3SiC{\equiv}C^-$: Green, D. C.; Englich, U.; Ruhlandt-Senge, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 354. (d) $Ph(Me_3Si)_2C^-$: Feil, F.; Harder, S. *Organometallics* **2000**, *19*, 5010. (e) $o\text{-MeO-}C_6H_4(Ar_2P)HC^-$: Knapp, V.; Müller, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 183. (f) $(C_6H_5)_3C^-$: Alexander, J. S.; Ruhlandt-Senge, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2658. (g) $o\text{-Me}_2N\text{-}C_6H_4(Me_3Si)CH^-$: Harder, S.; Feil, F.; Weeber, A. *Organometallics* **2001**, *20*, 1044. (h) $o\text{-Me}_2N\text{-}C_6H_4CH_2^-$: Harder, S.; Feil, F. *Organometallics* **2002**, *21*, 2268. (i) $p\text{-}t\text{-Bu-}C_6H_4CH_2^-$ and $C_6H_5CH_2^-$: Harder, S.; Müller, S.; Hübner, E. *Organometallics* **2004**, *23*, 178.

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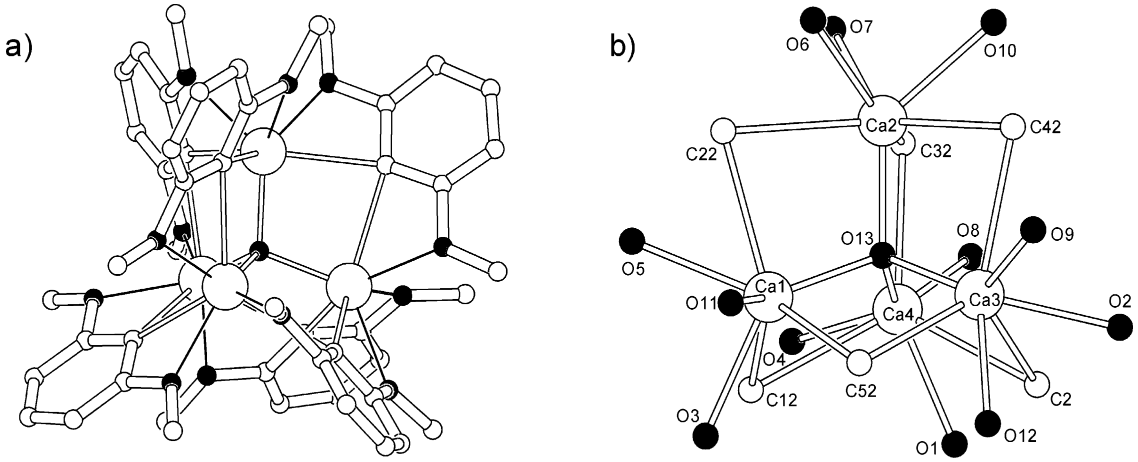

Figure 1. (a) Structure of the cluster (2,6-dimethoxyphenyl)$_6$Ca$_4$O. The oxygen atoms are depicted in black, and hydrogens atoms have been omitted for clarity. (b) Partial structure showing the coordination geometries for the calcium atoms and the numbering scheme.

Table 1. Calcium Coordination Spheres in the Ar$_6$Ca$_4$O Cluster[a]

Ca1–C12	2.748(3)	Ca2–C22	2.784(3)	Ca3–C2	2.766(3)	Ca4–C2	2.728(4)
Ca1–C22	2.753(4)	Ca2–C32	2.731(3)	Ca3–C42	2.774(4)	Ca4–C12	2.716(4)
Ca1–C52	2.785(4)	Ca2–C42	2.736(4)	Ca3–C52	2.750(4)	Ca4–C32	2.718(4)
Ca1–O13	2.128(2)	Ca2–O13	2.128(3)	Ca3–O13	2.132(2)	Ca4–O13	2.138(2)
Ca1–O3	2.399(3)	Ca2–O6	2.402(2)	Ca3–O2	2.399(2)	Ca4–O1	2.419(3)
Ca1–O5	2.415(2)	Ca2–O7	2.411(3)	Ca3–O9	2.393(2)	Ca4–O4	2.429(3)
Ca1–O11	2.402(2)	Ca2–O10	2.405(3)	Ca3–O12	2.421(3)	Ca4–O8	2.403(3)

[a] All values are given in Å; the numbering scheme is given in Figure 1b.

Ca$_4$O core is very close to T_d symmetry: Ca–O distances and Ca···Ca′ distances are in the very narrow ranges of 2.128(3)–2.138(3) and 3.468(1)–3.489(1) Å, respectively. The six dimethoxyphenyl anions bridge the six vertices of the tetrahedron: C$_{\text{ipso}}$ bridges two Ca^{2+} ions, and each methoxy group binds to one of the Ca^{2+} ions. All carbanions coordinate to the Ca$_4$O core in a similar fashion with similar Ca–C and Ca–O bond distances (Figure 1b; Table 1). Although the cluster shows high cubic symmetry, point group T with four C_3 axes along the Ca–O$_{\text{center}}$ bonds and three C_2 axes bisecting the Ca–O$_{\text{center}}$–Ca′ angles, all aryl rings are unique and no higher crystallographic symmetry could be found. The Ca–C bond distances in the cluster (average 2.749(4) Å) are much longer than Ca–C bonds in other σ-bonded organocalcium compounds (ranging from 2.459(9) Å[2b] to 2.649(2) Å[2d]), even when compared to bridging Ca–C bonds in dimers (2.561(3) Å).[2h] The long Ca–C bond distances are forced by the rather long Ca···Ca′ distances which are constrained by the central O atom. The Ca–OMe bonds vary from 2.393(2) to 2.429(3) Å (average 2.408(3) Å) and are somewhat longer than the average Ca–O distance of 2.328(2) Å in Ca^{2+}·6THF.[14] This is due to the strained four-membered chelate ring, which also causes strong deviations from the preferred trigonal coordination geometry of the ether oxygens, as indicated by the rather acute C$_{\text{ortho}}$–O–Ca angles (range 100.5(1)–103.4(1)°; average 102.2(1)°).

An interesting aspect of these new aryl complexes is that all aryl rings show a strong deformation from the regular hexagonal geometry, which can be described as arising mainly from C$_{\text{ipso}}$ being pulled out of the ring: the endocyclic angle at C$_{\text{ipso}}$ is squeezed, whereas those at the neighboring atoms are widened, as a necessary requirement to preserve ring planarity (Figure 2). It is known that a linear correlation exists between the

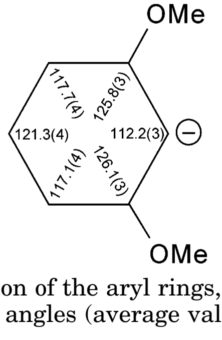

Figure 2. Distortion of the aryl rings, as shown by their endocyclic C–C–C angles (average values in degrees).

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(13) *Synthesis of (2,6-dimethoxyphenyl)potassium:* a solution of potassium 3-methyl-3-pentanolate (1.20 g, 8.57 mmol) in 10.0 mL of benzene was slowly added to a solution of (2,6-dimethoxyphenyl)-lithium[12] (1.10 g, 7.63 mmol) in a mixture of 5.0 mL of benzene and 0.5 mL of THF. Immediately a fine white precipitate formed. After it was stirred for 30 min, the reaction mixture was centrifugated and the precipitate was washed three times with 15 mL portions of benzene. Drying under high vacuum (0.01 Torr, 20 °C, 30 min) yielded the product as a white powder (1.21 g, 6.86 mmol, 90%). The compound is completely insoluble in THF but was characterized by quenching in CD$_3$OD, which gave complete conversion to 1-deuterio-2,6-dimethoxybenzene. ^{1}H NMR (C$_6$D$_6$/CD$_3$OD, 300 MHz): δ 3.33 (s, 6H), 6.45 (d, 8.1 Hz, 2H), 7.04 (t, 8.1 Hz, 1H). *Synthesis of [2,6-dimethoxyphenyl]$_6$-Ca$_4$O:* a mixture of (2,6-dimethoxyphenyl)potassium (2.10 g, 11.9 mmol) and CaI$_2$ (1.57 g, 5.34 mmol) was cooled to −50 °C, and 35 mL of THF was slowly added. The resulting suspension was stirred at room temperature for 72 h. The THF was removed under high vacuum, and the product was extracted from the remaining solid with three 15 mL portions of benzene. After removal of the benzene a white solid remained, which was washed with two 15 mL portions of hexane and subsequently dried under high vacuum (0.01 Torr, 20 °C, 30 min). The crude product (1.50 g) was dissolved in benzene, after which hexane was allowed to diffuse slowly into the solution. This resulted after 4 days in a crop of uniform needlelike crystals of [2,6-dimethoxyphenyl]$_6$Ca$_4$O (0.90 g, 0.90 mmol, 67% based on CaI$_2$). Anal. Calcd for (C$_8$H$_9$O$_2$)$_6$Ca$_4$O (M_r = 999.28): C, 57.69; H, 5.46. Found: C, 57.77; H, 5.79 (cf. Calcd for (C$_8$H$_9$O$_2$)$_2$Ca (M_r = 314.39): C, 61.13; H, 5.77). Melting point: 109 °C dec. ^{1}H NMR (THF-d_8, 300 MHz): δ(Ar$_6$Ca$_4$O) 3.25 (s, 3H), 6.29 (d, 7.9 Hz, 2H), 6.84 (t, 7.9 Hz, 1H); δ(Ar$_2$Ca) 3.35 (s, 3H), 6.16 (d, 2H, J = 7.8 Hz), 6.71 (t, 1H, J = 7.8 Hz). ^{13}C NMR (THF-d_8, 75.4 MHz): δ(Ar$_6$Ca$_4$O) 55.4, 103.6, 127.0, 151.5, 168.5; δ(Ar$_2$Ca) 54.8, 103.1, 127.7, 150.2, 168.1.

endocyclic angle at C_{ipso} and the electronegativity of the substituent: electronegative substituents result in a widening of the C−C−C angle, whereas electropositive substituents give rise to a squeezing.[15,16] The distortions observed in the aryl complexes of alkali metals are therefore extraordinary large[17] and can be explained by either hybridization effects or by simple VSEPR theory: [15] i.e., the C−M electron pair is strongly polarized toward the carbon, resulting in considerable repulsion with the $C_{ipso}-C_{ortho}$ electron pairs. The extent of these distortions directly correlates to the ionicity of the C−M bond. Therefore, comparison of the aryl ring distortions observed in the present arylcalcium complex with those in (2,6-dimethoxyphenyl)lithium enables an indirect comparison of C−Li and C−Ca bond polarity. The average C−C−C angle at C_{ipso} amounts to 112.2(3)° in the present compound, which compares well to the average value of 112.6(5)° for the lithium analogue.[18] The ionicity of the C−Ca bond is therefore comparable to that of a C−Li bond.

Crystals of the Ar_6Ca_4O cluster are insoluble in benzene but can be dissolved in THF; however, a very small amount of a white solid precipitates again after dissolution. ^1H and ^{13}C NMR spectra of the THF solution show two sets of signals in an approximate ratio of 1:2.5. Therefore, at least two different species must be present in solution. The ratio of both species is initially 1:2.5 but changes over time, and after several days only one species is present. The ^{13}C chemical shifts for the C_{ipso} atoms are rather large (150.2 and 151.5 ppm), indicating that both species contain the 2,6-dimethoxyphenyl anion. We therefore conclude that the Ar_6Ca_4O cluster in THF slowly decomposes in Ar_2Ca and CaO, the latter precipitating from solution.

The Ar_6Ca_4O cluster is another example of oxygen scavenging by polar organometallic clusters, in which there is increasing interest.[19−22] Although oxide-contaminated organometallics are usually accidental products, the synthesis of the current Ar_6Ca_4O cluster and its analyses (X-ray, NMR, and elemental analysis) are reproducible. Reproducible synthetic strategies also have been developed for a class of compounds called "inverse crown ethers" (a ring of metal ions surrounding the encapsulated O^{2-} ion).[20,21] In analogy, the Ar_6Ca_4O cluster could be seen as an "inverse cryptand", for which several precedents have been observed in lithium chemistry.[22] Interestingly, the crystal structure of Ar_6Li_8O, likewise with the 2,6-dimethoxyphenyl carbanion, is one of these examples.[23] Nearly all scavenger lithium clusters show an O^{2-} ion in the middle of an octahedron spanned by six Li^+ ions.[22] The present structure shows the O^{2-} ion in the middle of a tetrahedron spanned by four Ca^{2+} ions. This is likely due to the larger radius and higher charge of Ca^{2+} in comparison to Li^+, thus enforcing larger M−O−M angles and longer M···M distances.

In most oxygen scavenger complexes the origin of the encapsulated O^{2-} ion is unclear.[22] For the present system there are three possible oxygen sources: (i) H_2O or O_2 leaked in from the atmosphere, (ii) the carbanion 2,6-dimethoxyphenyl, and (iii) THF cleavage. The fact that crystals of the benzene-insoluble Ar_6Ca_4O cluster grow from a benzene solution of the crude product indicates that the oxide is formed during the crystallization process. Since the crude product does not contain THF, oxide formation by THF cleavage is impossible here. GC-MS analysis of the mother liquor after crystallization did not reveal any products that point to elimination reactions involving the MeO substituents but clearly showed the presence of 2,2′,6,6′-tetramethoxybiphenyl. It is therefore likely that, despite careful Schlenk techniques, oxidation of Ar_2Ca into Ar−Ar and CaO occurred. Slow generation of CaO resulted in slow formation of the highly symmetrical benzene-insoluble Ar_6Ca_4O cluster, which under these conditions crystallized nicely.

The structure of the present Ar_6Ca_4O cluster contains a Ca_4O unit which shows a striking resemblance with the Zn_4O unit in $[O^{-}(O)CC_6H_4C(O)O^{-}]_3Zn_4O$ (MOF-5),[24] the prototype of the MOF systems that recently received considerable attention as hydrogen storage systems.[25] This suggest that lighter MOF materials based on calcium might be feasible as well.

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Supporting Information Available: Information on the crystal structure determination, including a CIF file and an ORTEP plot of the crystal structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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