Organocalcium Compounds

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THF Solvates of Extremely Soluble Bis(2,4,6-trimethylphenyl)calcium and Tris(2,6-dimethoxyphenyl)dicalcium Iodide**

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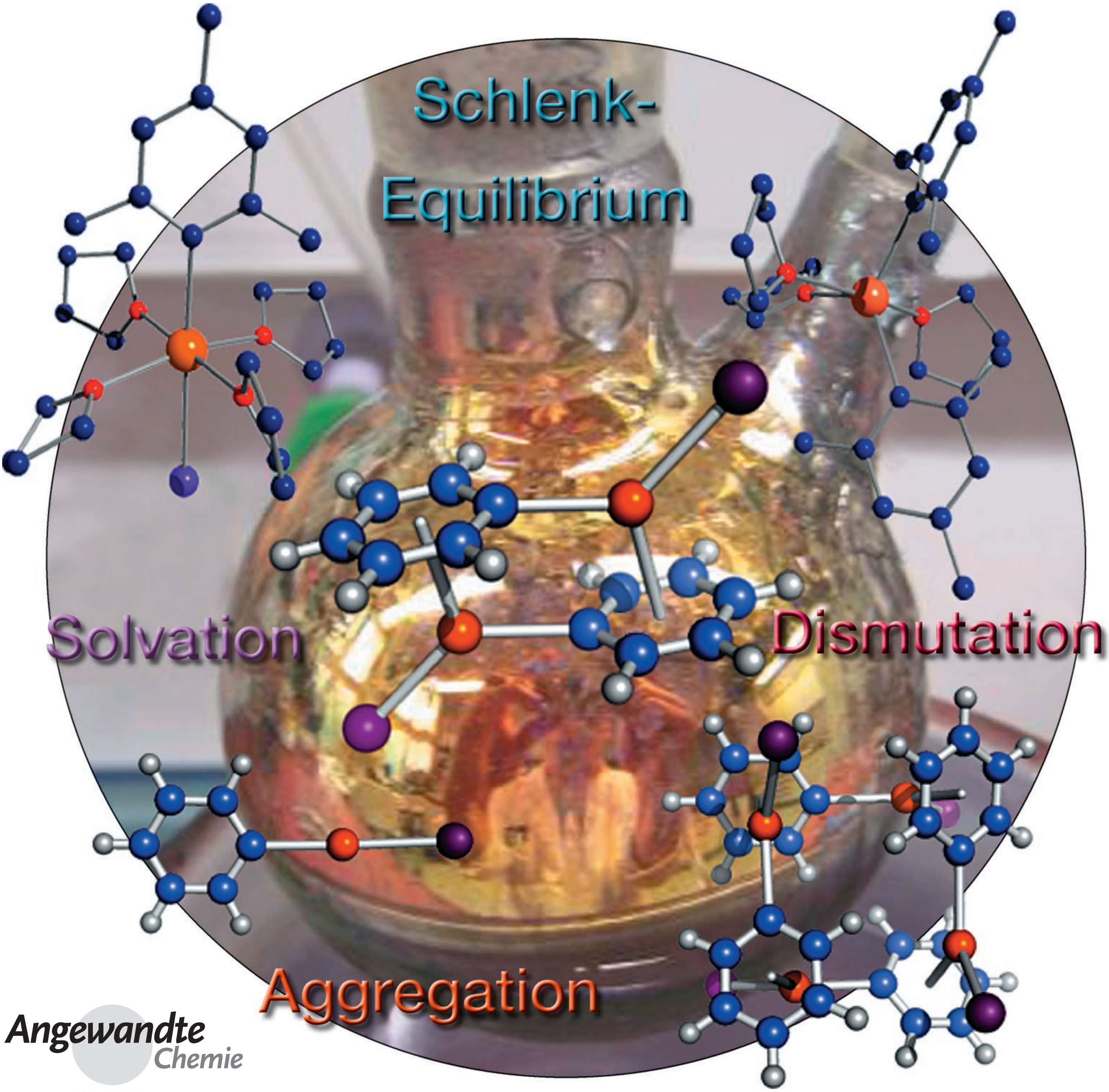
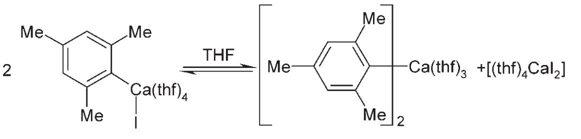


The chemistry of the heavy alkaline-earth metals is still in its early stages whereas organomagnesium[1] and organo-alkali-metal chemistry[2] exhibit a long tradition. The direct synthesis of aryl calcium iodides proceeds smoothly after activation of calcium metal in liquid ammonia.[3] These aryl calcium compounds show a very high reactivity and tend to cleave ether solvents already above −35 °C.[4] Ether and substrate cleavage by aryl calcium compounds yield oxygen-centered cages such as $[\{2,6\text{-}(MeO)_2C_6H_3\}_6Ca_4O]$ (av Ca−C 275 pm)[5] and $[\{(thf)_2CaPhI\}_3{\cdot}(thf)CaO]$ (av Ca−C 259 pm)[4] with central Ca_4 tetrahedrons. During these side reactions, methyl groups in the *ortho* position can be deprotonated and benzylcalcium derivatives are thereby obtained.[6] Consequently, aryl calcium halides have to be handled and stored at low temperatures. Niemeyer and co-workers[7] isolated a sterically shielded pentafluorophenylcalcium triazenide with a Ca−C bond length of 249.9(11) pm. The incorporation of the aryl moiety into a crown ether as in 2-(phenylcalcio)-1,3-xylylene-[18]crown-5 also enhanced the thermal stability, but owing to low solubility the characterization had to be performed through derivatization.[8] The cocondensation of calcium with benzene and alkyl benzenes yielded aryl calcium hydrides by insertion of a calcium atom into a C−H bond.[9] However, neither NMR data nor structural parameters have been determined. For mesitylcalcium iodide two sets of resonances were observed in the NMR spectra and were interpreted in the sense of a Schlenk equilibrium [Eq. (1)].[6] Thus far, a diaryl calcium derivative has never been structurally characterized.



1 (1)

Slow fractionated crystallization of a mesitylcalcium iodide solution afforded $[(thf)_4CaI_2]$ at temperatures between −30 and −50 °C. After removal of the dihalide, storage of the solution at −78 °C for several days led to the precipitation of $[(thf)_4Ca(Mes)I]$ (Mes = 2,4,6-$Me_3C_6H_2$). After reduction of the volume of the filtrate the very concentrated and viscous mother liquor was stored at −90 °C, which led to the crystallization of $[(thf)_3CaMes_2]$ (**1**). This diaryl calcium compound is much more reactive than the aryl calcium iodide and cleaves ether already above −55 °C, which required the isolation and handling of these crystals at very low temperatures. The extreme solubility of aryl calcium derivatives in THF is in striking contrast to earlier investigations of organocalcium compounds, which often had to be characterized by derivatization owing to insolubility in common organic solvents.

The molecular structure of **1** is represented in Figure 1. The molecule shows a C_2-symmetric structure with the mesityl groups in the equatorial plane. Owing to the small coordination number of five, the Ca−C1 bond length (252.0(3) pm) is rather small. In $[(thf)_4Ca(Mes)I]$, with a metal center in an octahedral environment, a Ca−C bond length of 257.4(4) pm was observed.[6] Owing to steric reasons, the axial Ca−O1 bond length of **1** (241.1(2) pm) is significantly larger than the equatorial Ca−O2 bond (236.7(3) pm). Whereas the angles within the equatorial plane lie rather close to 120°, distortions are observed for the axial thf ligands. The bulky mesityl groups bend these ligands toward the smaller equatorial thf base, thus causing the O1-Ca-O1′ and O1-Ca-O2 angles to be 159.5(1)° and 79.76(6)°, respectively.

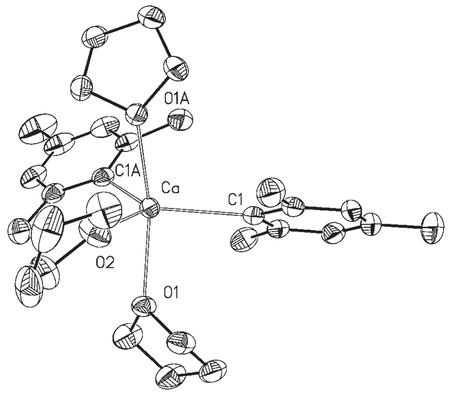


Figure 1. Molecular structure of **1**. Ellipsoids are shown at 40% probability; H atoms are omitted for clarity. Symmetry-equivalent atoms are denoted with an A ($-x+1$, y, $-z+0.5$). Selected bond lengths [pm] and angles [°]: Ca-C1 252.0(3), Ca-O1 241.1(2), Ca-O2 236.7(3);: Ca-C1-C2 125.6(2), Ca-C1-C6 120.8(2), C2-C1-C6 113.7(3), C1-Ca-O1 89.10(9), C1-Ca-O2 120.21(8), C1-Ca-O1A 101.23(9), O1-Ca-O1A 159.5(1), O1-Ca-O2 79.76(6).

Incorporation of a Lewis base into the *ortho* substituents should influence the Schlenk equilibrium. Therefore, calcium powder was treated with 1-iodo-2,6-dimethoxybenzene. Cooling of this solution led to the formation of crystalline $[(thf)_4CaI_2]$ and aryl-rich $[(thf)_2Ca\{\mu\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2\}_3Ca(thf)I]$ (**2**) in a rather poor yield. Therefore, 1,3-dimethoxybenzene was deprotonated with phenylcalcium iodide and

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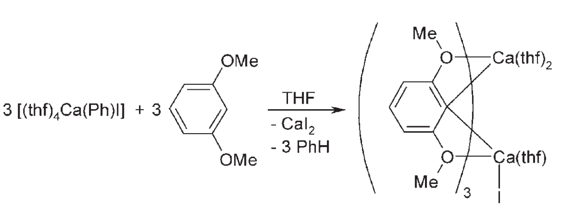
from this solution the dinuclear complex **2** was isolated according to Equation (2).



(2)

2

The molecular structure of **2** is displayed in Figure 2. The calcium atoms are bridged by three aryl ligands whereas the iodine atom is in a terminal position (CaB–I 330.6(1) pm). The eight-coordinate calcium atoms show an average Ca–C bond length of 269.8 pm. Owing to the chelating effect of the 2,6-dimethoxyphenyl groups, a short Ca···Ca contact (333.4(2) pm) is observed. The Ca–O distances of the methoxy fragments and of the thf ligands lie in the same range.

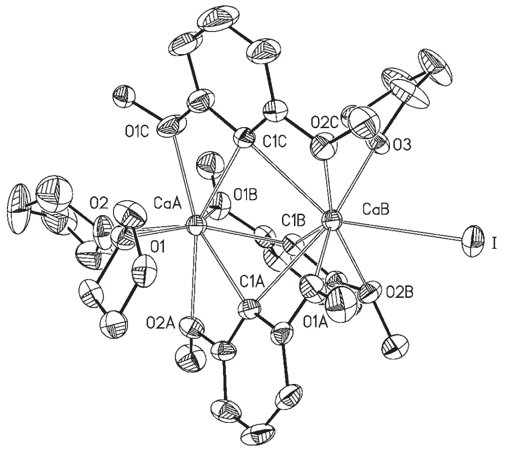


Figure 2. Molecular structure of **2**. Ellipsoids are shown at 40% probability; H atoms are omitted for clarity. Selected bond lengths [pm]: CaA-C1A 261.3(6), CaA-C1B 271.5(6), CaA-C1C 267.8(5), CaB-C1A 275.0(6), CaB-C1B 269.6(5), CaB-C1C 273.4(6), CaB-I 330.6(1), CaA-O1 246.9(4), CaA-O2 251.5(4), CaA-O1B 247.6(4), CaA-O1C 240.9(4), CaA-O2A 249.5(4), CaB-O3 242.4(4), CaB-O1A 248.6(4), CaB-O2B 243.9(4), CaB-O2C 241.5(4), CaA···CaB 333.4(2).

Concentration of the aryl calcium iodide solutions led to oily residues. From NMR spectroscopic data it was concluded that the THF content was too low to dissolve the aryl calcium derivatives as monomeric THF adducts. However, we were unable to isolate crystalline oligomeric aryl calcium compounds suitable for X-ray diffraction experiments.[10]

To investigate possible structures of oligomeric aryl calcium iodides and diaryl calcium compounds with respect to solvent effects, the solvation energy (coordination of four ether molecules to PhCaI and Ph_2Ca) and the dimerization as well as tetramerization of PhCaI and Ph_2Ca were investigated with quantum chemical calculations[11] (see the Supporting Information for details). DFT calculations (BP86/TZVPP) show that the coordination of four ether molecules to the calcium atom provide a structure in good agreement with the X-ray structure of $[(thf)_4Ca(Ph)I]$.[3] Coordination of ether molecules is associated with strong exothermic energies ($[(Me_2O)_nCa(Ph)I]$: $n=1$, -62.3; $n=2$, -150.4; $n=3$, -189.1; $n=4$, $-227.2\ kJ\,mol^{-1}$). The four possible dimer structures of PhCaI and their corresponding energies obtained with BP86/TZVPP, B3LYP/TZVPP, and MP2/RI/TZVPP are shown in Figure 3. The data and structures shown also allow us to understand the coordination modes of the phenyl rings in Ph_2Ca. The largest rearrangement energy is about $-50\ kJ\,mol^{-1}$ in DFT calculations (this value is almost independent of the density functional chosen), while MP2 calculations yield $-116\ kJ\,mol^{-1}$. Since MP2 is able to describe the contribution of dispersion interactions to the π system of the phenyl groups coordinating to calcium atoms, we may assume that the MP2 results provide a better estimate in this case. Furthermore, as shown by the data in Figure 4, the dimerization of linear PhCaI (and analogously of Ph_2Ca) to the most stable structure depicted in Figure 3 leads to a stabilization of about $-200\ kJ\,mol^{-1}$ from the DFT calculations. This value is about half of the solvation energy of in total eight ether molecules solvating two monomers. Nevertheless, the dimerization energy is of the same order as the solvation energy because of the dispersion contributions neglected in DFT, which favor the dimerization additionally by about $77\ kJ\,mol^{-1}$ (as estimated by comparison with the MP2 data obtained for the dimerization; see Figure 4). Moreover, the solvation of the dimeric structure by ether molecules, which has not been considered here, would also favor the dimerization process compared to the solvation of the monomer. We emphasize that PhCaI and Ph_2Ca behave very similarly. Surprisingly, the bridging σ-bound phenyl groups are coordinated in a η^6 mode to the other calcium atom; for PhCaI the energy gained from this coordination can

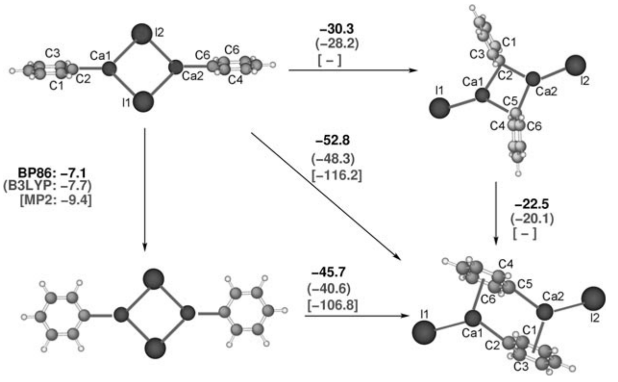


Figure 3. BP86/TZVPP-optimized dimer structures and corresponding electronic energy differences [$kJ\,mol^{-1}$] at 0 K. Energy differences from B3LYP/TZVPP optimizations are given in parentheses. For comparison, energy differences from single-point MP2/RI/TZVPP calculations are given in brackets. From the data shown one can grasp the energetics of the different coordination modes of the iodine ligand and the phenyl ring. It was not possible to optimize the structure in the upper right corner with MP2.

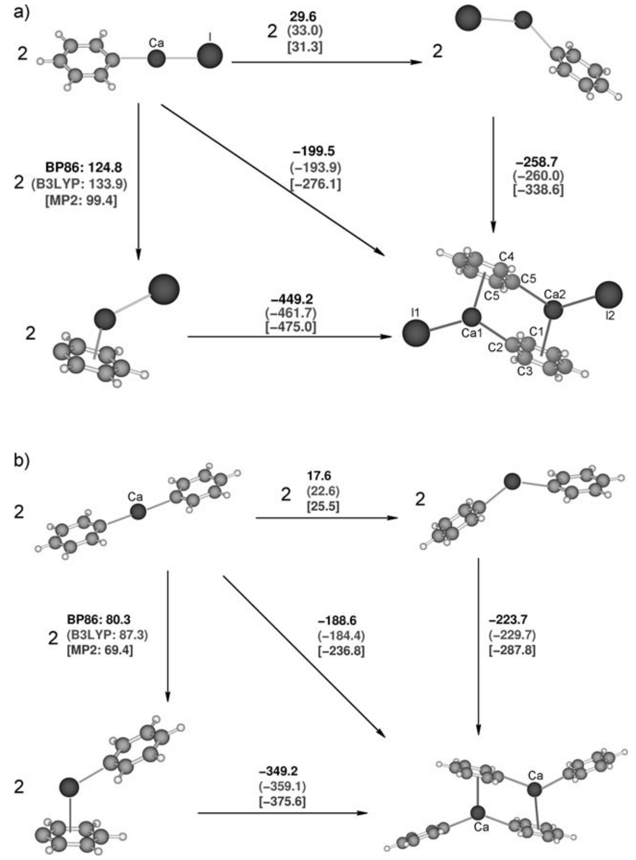


Figure 4. Electronic-energy differences [kJ mol^{-1}] for the formation of the PhCaI (top) and Ph$_2$Ca (bottom) dimers at 0 K from BP86/TZVPP and B3LYP/TZVPP (in parentheses) calculations. Energy differences of single-point MP2/RI/TZVPP calculations are given in brackets. The overall trends are very similar for both systems, although the absolute values of the reaction energies are consistently smaller for Ph$_2$Ca when compared with PhCaI. The factor of 2 on some reaction arrows denotes that the energy is given per monomer but must be multiplied by two for dimerization.

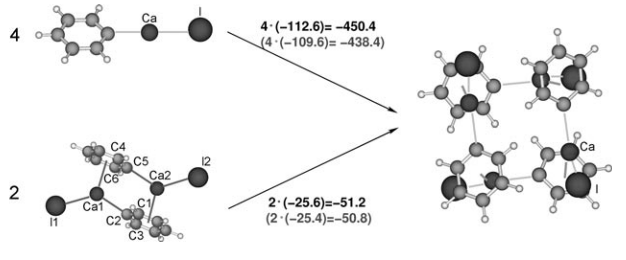


Figure 5. Electronic-energy differences [kJ mol^{-1}] for the formation of the cyclic tetramer of PhCaI obtained in BP86/TZVPP and B3LYP/TZVPP structure optimizations (given in parentheses) at 0 K.

be estimated to be at least 130 kJ mol^{-1} (DFT) up to 170 kJ mol^{-1} (MP2), with the latter result being more accurate for the reason given above. Moreover, this structural motif can be extended to the formation of a tetramer (Figure 5), which again is exothermic by a value of about −25 kJ mol^{-1} per dimer if solvation-free isolated structures are considered. In this S_4-symmetric tetramer the alkaline-earth-metal atoms are shielded quite effectively and a further oligomerization seems to be disadvantageous.

The tendency of calcium cations to bind to π-electron systems has been shown experimentally for the benzylcalcium derivatives[12] and metallocenes.[13,14] Furthermore, in calcium 2,6-diphenylphenolates coordination vacancies at calcium are occupied by π-bonded pendant phenyl groups.[15] Compounds with a stabilization by side-on coordination of arenes to the isoelectronic potassium cation[16] and to lanthanoids[17] are well-known. Theoretical studies support the strength of the interactions between calcium and neutral arene π systems.[18]

The diaryl calcium compounds are extremely reactive and cleave ether already above −55 °C. Therefore, it cannot be ruled out that the reactivity of the aryl calcium iodides is caused by the formation of this diaryl calcium species. In contrast to earlier reports the extreme solubility in common organic solvents is striking, and on the basis of quantum chemical calculations a dimerization and tetramerization are suggested. These oligomers again seem to be very soluble in ether solvents such as THF.

Experimental Section

All manipulations were carried out in an anhydrous argon atmosphere. The solvents were thoroughly dried and distilled in an argon atmosphere. Calcium was activated prior to use.[3] 1-Iodo-2,6-dimethoxybenzene was prepared according to a literature procedure.[19] 1,3-Dimethoxybenzene was dried and distilled over CaH$_2$ prior to use.

1: A 500-mL Schlenk flask with glass balls (diameter 5 mm), activated calcium (3.4 g, 85.0 mmol), and THF (150 mL) was cooled to −78 °C. Iodo-2,4,6-trimethylbenzene (13.0 g, 52.8 mmol) was added and the flask was shaken for 5 h. During this time the temperature was kept below −50 °C. The glass balls, the excess of calcium metal, and a part of precipitated [CaI$_2$(thf)$_4$] were removed below −30 °C, and the filtrate (86 % yield of organocalcium compound as calculated by acid consumption of an aliquot) was kept for 4 days at −78 °C. The colorless precipitate of [MesCaI(thf)$_4$] (11.2 g, 19.5 mmol, 37.0 %) was collected on a cooled frit and dried in vacuo. The yellow filtrate was concentrated in a cooling bath below −30 °C under reduced pressure to one third of its original volume and kept overnight at −90 °C. Colorless crystals grew in an oily mother liquor. The iodide-free crystals were decanted from the mother liquor and dried in vacuo at −55 °C. Yield: 1.58 g, 4.1 mmol, 15.4 %.

2 by direct synthesis: A Schlenk flask with activated calcium (1.50 g, 37.4 mmol), glass balls (diameter 5 mm, 50 g), and THF (50 mL) was cooled to 0 °C. 1-Iodo-2,6-dimethoxybenzene (4.94 g, 18.7 mmol, 0.5 equiv) was added slowly. The flask was shaken for one hour at 0 °C and an additional six hours at ambient temperature. The resulting suspension was filtered and the yield of 56 % was determined by acidic consumption of a hydrolyzed aliquot; using a longer reaction time of 14 h raised the yield to 67 %. Overnight cooling of this solution to −90 °C gave colorless crystals, which were collected and dried in vacuo. Repeated crystallization of this substance gave crystalline compound **2** and a precipitate of [(thf)$_4$CaI$_2$].

2 by directed *ortho* metalation: A solution of phenylcalcium iodide (2.15 g, 4.03 mmol) in 1,3-dimethoxybenzene (5.57 g, 40.3 mmol, 10 equiv) was stirred at 50 °C. During the reaction, liberated THF and benzene were distilled off continuously under reduced pressure. After 15 minutes a colorless precipitate began to form. After one hour the reaction mixture was cooled to ambient temperature. The precipitate was collected, washed with 1,3-dimethoxybenzene (2 × 5 mL), and dried in vacuo. The remaining solid was dissolved in THF and the yield was determined to be 83 % (3.33 mmol) by acidic consumption of a hydrolyzed aliquot. Cooling of this solution to 10 °C led to precipitation of $[(thf)_4CaI_2]$ and to crystallization of **2** at the walls of the Schlenk flask.

2: ^{1}H NMR (400.3 MHz, $[D_8]$THF, 25 °C): $\delta = 3.68$ (s, 3H, CH_3O), 3.70 (s, 3H, CH_3O), 6.39 (d, 2H, $^3J_{H,H} = 7.6$ Hz, H3 and H5), 6.91 ppm (t, 1H, $^3J_{H,H} = 6.1$ Hz, H4); $^{13}C\{^1H\}$ NMR (100.6 MHz, $[D_8]$THF, 25 °C): $\delta = 56.8$ (CH_3O), 103.9 (C3 and C5), 127.5 (C4), 152.0 (C1), 167.9 ppm (C2 and C6).

X-ray structure determination of **1** and **2**: The intensity data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. Data were corrected for Lorentz polarization and for absorption effects.[20–22] The structures were solved by direct methods (SHELXS[23]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[24]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms except for the disordered solvent molecules were refined anisotropically.[24] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal data for **1**:[25] $C_{30}H_{46}CaO_3$, $M_r = 494.75$ g mol^{-1}, colorless prism, $0.06 \times 0.06 \times 0.04$ mm^3, orthorhombic, space group $Pbcn$, $a = 10.1514(7)$, $b = 15.2540(14)$, $c = 19.3887(19)$ Å, $V = 3002.3(5)$ Å^3, $T = -90$ °C, $Z = 4$, $\rho_{calcd} = 1.095$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 2.35$ cm^{-1}, multiscan, min./max. transmission: 0.6585/0.9820, $F(000) = 1080$, 11 509 reflections in $h(-12/13)$, $k(-16/19)$, $l(-25/21)$, measured in the range $2.10° \leq \Theta \leq 27.35°$, completeness $\Theta_{max} = 97.3\,\%$, 3307 independent reflections, $R_{int} = 0.0760$, 1803 reflections with $F_o > 4\sigma(F_o)$, 158 parameters, 0 restraints, $R1_{obs} = 0.0654$, $wR^2_{obs} = 0.1464$, $R1_{all} = 0.1369$, $wR^2_{all} = 0.1836$, GOF = 1.019, largest difference peak and hole: 0.319/−0.261 e Å^{-3}.

Crystal data for **2**:[25] $C_{36}H_{51}Ca_2IO_9$, $M_r = 834.83$ g mol^{-1}, colorless prism, $0.07 \times 0.07 \times 0.05$ mm^3, triclinic, space group $P\bar{1}$, $a = 10.6955(9)$, $b = 10.9592(7)$, $c = 17.4528(13)$ Å, $\alpha = 95.758(4)$, $\beta = 92.557(4)$, $\gamma = 108.029(4)°$, $V = 1929.3(2)$ Å^3, $T = -90$ °C, $Z = 2$, $\rho_{calcd} = 1.437$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 11.45$ cm^{-1}, multiscan, min./max. transmission: 0.6585/0.8820, $F(000) = 864$, 11 443 reflections in $h(-13/13)$, $k(-/14)$, $l(-21/22)$, measured in the range $2.64° \leq \Theta \leq 27.53°$, completeness $\Theta_{max} = 89.2\,\%$, 7930 independent reflections, $R_{int} = 0.0500$, 4323 reflections with $F_o > 4\sigma(F_o)$, 433 parameters, 0 restraints, $R1_{obs} = 0.0619$, $wR^2_{obs} = 0.1320$, $R1_{all} = 0.1402$, $wR^2_{all} = 0.1658$, GOF = 1.014, largest difference peak and hole: 0.813/−0.715 e Å^{-3}.

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[10] To study the solvent dependency of the Schlenk equilibrium, $[(Et_2O)_4Ca(Ph)I]$ was prepared in diethyl ether. Upon cooling of this solution $[(Et_2O)_4CaI_2]$ precipitated and Ph_2Ca remained in solution. However, ether cleavage and the formation of $[\{(Et_2O)CaPh_2\}_4{\cdot}(Et_2O)CaO]$ with an oxygen-centered Ca_5 square pyramid was observed.

[11] Computational methodology: All Kohn–Sham DFT (with the BP86 and B3LYP density functionals) and ab initio MP2 calculations were performed with the quantum chemical program package Turbomole (R. Ahlrichs et al., http://www.cosmologic.de/turbomole.html). For details on the methodology and the basis sets used, see the Supporting Information. For the calculation of partial charges, we applied a modified Löwdin analysis. See also: a) A. E. Clark, E. R. Davidson, *J. Chem. Phys.* **2001**, *115*, 7382–7392; b) C. Herrmann, M. Reiher, B. A. Hess, *J. Chem. Phys.* **2005**, *122*, 34102.

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[25] CCDC-624777 (**1**) and CCDC-624778 (**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.