Reactivity studies of phenylcalcium iodide towards THF yielding phenyl-free cage compounds – Crystal structures of [{(thf)Ca(O–CH=CH$_2$)$_2$}$_4$ · CaO · CaI$_2$] and [(CaO)$_4$ · 4 (thf)$_3$CaI$_2$]

Sven Krieck, Helmar Görls, Matthias Westerhausen *

Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, August-Bebel-Str. 2, D-07743 Jena, Germany

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ABSTRACT

THF proved to be the favoured solvent for the direct synthesis of phenylcalcium iodide. However, ether degradation is the major side reaction in this solvent. Zinc-mediated degradation of THF leads to the formation of the cage compound [{(thf)Ca(O–CH=CH$_2$)$_2$}$_4$ · CaO · CaI$_2$] (**1**) besides the zincate [(thf)$_6$Ca][ZnEt$_2$Ph$_2$]. The structure of **1** shows an oxygen-centered Ca$_6$ octahedron with iodine atoms bound to two opposite corners. Heating of phenylcalcium iodide in THF solution for several hours yields [(CaO)$_4$ · 4 (thf)$_3$CaI$_2$] (**2**) with a central Ca$_4$O$_4$ heterocubane unit. NMR monitoring of the reaction shows that the phenyl groups are converted to benzene due to α-deprotonation of THF.

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1. Introduction

Working with post-Grignard reagents poses several challenges which hampered the development of the organocalcium chemistry such as the discrepancy between the low reactivity of the metal itself and the high reactivity of the organocalcium compounds. Whereas the organomagnesium chemistry quickly found the interest of many research laboratories and entrance in many applications as Grignard reagents, contrary reports on the synthesis and behaviour of organocalcium reagents (post-Grignard reagents) were puzzling and needed justification. First reports on arylcalcium halides date back to 1905 when Beckmann [1] performed the direct synthesis of calcium with aryl halides. Gilman and Schulze [2] reinvestigated this reaction in detail and found that Beckmann probably isolated the ether complex of calcium(II) iodide instead of an organocalcium compound. They also noticed that the yields of RCaI were far from satisfactory due to C–C bond formation (Wurtz-type coupling reactions). They also observed that organocalcium iodides were less reactive than RMgX.

Bryce-Smith and Skinner [3] stated that also Gilman and Schulze might have been wrong because they underestimated the importance of ether cleavage reactions in the chemistry of organocalcium compounds and because they employed inappropriate analytical methods which were unable to differentiate between organocalcium compounds and certain ether cleavage products. Despite the investigations of Bryce-Smith and Skinner, contrary reports were published regarding the stability of arylcalcium derivatives in solution and in the solid state. On the one hand, the preparation of PhCaI was performed in hot Et$_2$O [4], treatment of its 1,4-dioxane adduct at 110 °C led to loss of coordinated ether and to formation of high-melting PhCaI [5,6]. The synthesis of diphenylcalcium was performed in boiling ether from Ca and HgPh$_2$ within 25 h [7], higher yields up to 92% were achieved in THF solution [7,8]. Thereafter, CaPh$_2$ was used to deprotonate fluorene, triphenyl- and diphenylmethane [9]. On the other hand, Markies et al. noticed that diphenylcalcium showed a very limited stability in THF solutions which afforded synthesis and handling at very low temperatures [10]. Therefore, they used freshly prepared solutions immediately for bromine–calcium exchange reactions. Excessive ether cleavage was also observed during the reactions of e.g. PhCaBr with 1,3-benzoxathiole and 1,3-benzodioxole [11]. In the last few years numerous crystal structures were presented containing oxygen-centered calcium cages such as [{Ca(C$_6$H$_3$-2,6-

{OMe}$_2$)$_2$)$_3$ · CaO] [12], [{(thf)$_2$Ca(Ph)I}$_3$ · (thf)CaO] [13], and [{(Et$_2$O)CaPh$_2$}$_4$ · (Et$_2$O)CaO] [14]. THF cleavage was also observed for mesitylcalcium iodide [15] and other arylcalcium halides [16]. A detailed study of THF degradation with naphthylcalcium bromide showed that the first reaction step was the α-deprotonation of the THF molecule, followed by the formation of ethene and vinylalcoholate. However, the amount of vinylalcoholate decreased again after a few hours at room temperature and derivatization reactions of the residue suggested the formation of calcium acetylide [17].

Another challenge was the identification of arylcalcium halides and their differentiation from other by-products. In the beginning of the research on organocalcium halides, RH was often identified after protolysis of RCaX with water or acids in order to determine the yields [4,18,19]. Due to ether cleavage reactions, the amount of RH was enhanced as a consequence of α-deprotonation reactions of RCaX with the solvent THF. Therefore, it is advisable to determine the amount of organocalcium halides *via* titration after decomposition of these post-Grignard reagents with chloroform [20].

In all these degradation reactions of THF the formation of vinylalcoholate species was observed by NMR spectroscopy. However, a simple complex was neither isolated nor structurally characterized. Nevertheless, Bradley et al. [21] as well as Ruhland-Senge and coworkers [22] observed cleavage of crown ether by alkaline earth metal bis[bis(trimethylsilyl)amides]. Oxygen-centered alkaline earth metal cages were also found in the alcoholate chemistry [23]. The degradation of intermediate vinylalcoholate was detected by NMR spectroscopy and resulting CaO was trapped by still present post-Grignard reagent leading to the formation of oxygen-centered calcium polyhedrons such as a Ca$_4$ tetrahedron [12,13] or a square Ca$_5$ pyramid [14]. However, these compounds are also very reactive and tend to cleave ether at room temperature or higher temperatures. Therefore, we investigated the degradation of arylcalcium iodide in THF at elevated temperatures.

2. Results

2.1. Synthesis

From the observations discussed above it was assumed that several reactions occur at the same time. On the one hand THF cleavage leads to the formation of vinylate anions which can also be deprotonated yielding oxygen-centered cage compounds. On the other hand, the formation of these cages traps still existing post-Grignard reagent and the reactivity of these phenylcalcium fragments is reduced. In order to separate the dominant degradation products, namely the firstly formed vinylate and the final CaO-containing species, a strategy has to be developed to accelerate vinylate formation without acceleration of its degradation by still present phenylcalcium compounds.

In order to achieve a complete degradation of phenylcalcium iodide and its vinylalcoholate intermediates, a THF solution of PhCaI was heated under reflux in order to destroy also all oxygen-centered cage compounds of the type [{(thf)$_2$Ca(Ph)I}$_3$ · (thf)CaO] [13]. During prolonged heating samples were taken regularly and the basicity was determined by titration. It was also observed in the NMR spectrum that the concentration of phenyl groups decreased and that the amount of benzene increased. After complete conversion of the phenyl groups into benzene *via* ether cleavage we were able to isolate a phenyl-free octa-nuclear cage compound of the type [(CaO)$_4$ · 4 (thf)$_3$CaI$_2$] (**1**) with a central Ca$_4$O$_4$ heterocubane moiety (Eq. (1)).

(1)
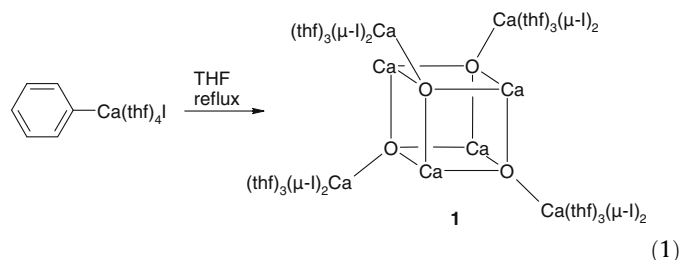
In order to isolate the intermediate the formation of vinylate anions has to be accelerated without acceleration of its degradation i.e. at low temperature. The reactivity of organylcalcium compounds can be enhanced by addition of diethylzinc [24]. Thus CaZnR$_4$ showed a higher reactivity than homoleptic CaR$_2$ and ZnR$_2$ in reactions with ketones [25]. Therefore, we added dialkylzinc to a phenylcalcium iodide solution in THF in order to increase the degradation rate at rather low temperatures. This procedure allowed the isolation of the vinylalcoholate species. Thus from a 2:1 mixture of PhCaI and ZnEt$_2$ a microcrystalline solid precipitated which showed a 1:1 ratio of Ca:Zn and a ratio of 3:1:1 for THF:Et:Ph giving a formula of [(thf)$_6$Ca] [ZnEt$_2$Ph$_2$]. From the mother liquor of this reaction a hexa-nuclear phenyl-free cage compound of the formula [{(thf)Ca(O–CH=CH$_2$)$_2$}$_4$ · CaO · CaI$_2$] (**1**) was isolated as shown in Eq. (2).

(2)
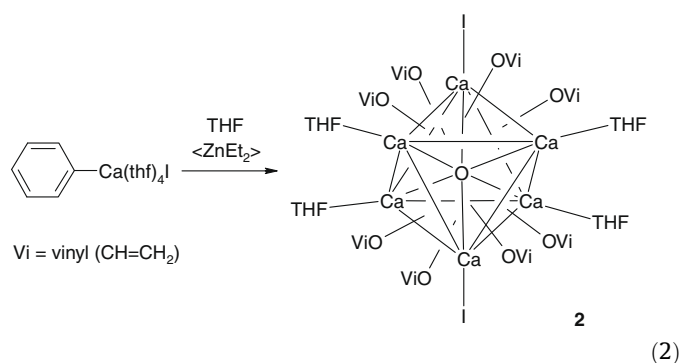
Due to disordering of the vinyl groups the e.s.d. values of the C–C bond lengths are rather large. Therefore the nature of this group (vinyl vs. ethyl) was clarified with NMR experiments. The ^{13}C NMR shifts of δ = 68.7 (CH$_2$) and δ = 91.5 (CH) clearly support a C=C double bond. In the ^{1}H NMR spectrum, the coupling pattern and the chemical shifts also verify the existence of vinyl groups and the absence of ethyl groups. These NMR parameters are in agreement with reported data for comparable compounds produced by cleavage of THF (vinylalcoholates of Sc [26] and Y [27]). In addition the C=C stretching mode of 1615 cm^{-1} in the IR spectrum shows the existence of C=C multiple bonds of a vinylate, the bands at 887 and 1035 cm^{-1} are characteristic for coordinated THF molecules and in agreement with literature values of a vinylalcoholate of La [28].

2.2. Molecular structures

Molecular structure and numbering scheme of [(CaO)$_4$ · 4 (thf)$_3$CaI$_2$] (**1**) are presented in Fig. 1. The central unit consists of a Ca$_4$O$_4$ heterocubane structure which represents a small cut-out of the calcium oxide structure. Due to a strong electrostatic attraction between the ions Ca^{2+} and O^{2-} the distances vary between 2.223(9) and 2.292(8) Å. Additional (thf)$_3$CaI$_2$ molecules bind to these oxide anions with extremely short Ca3–O2 and Ca4–O1 bond lengths of 2.158(8) Å. The iodine atoms occupy bridging positions between an inner and an outer calcium atom. The inner penta-

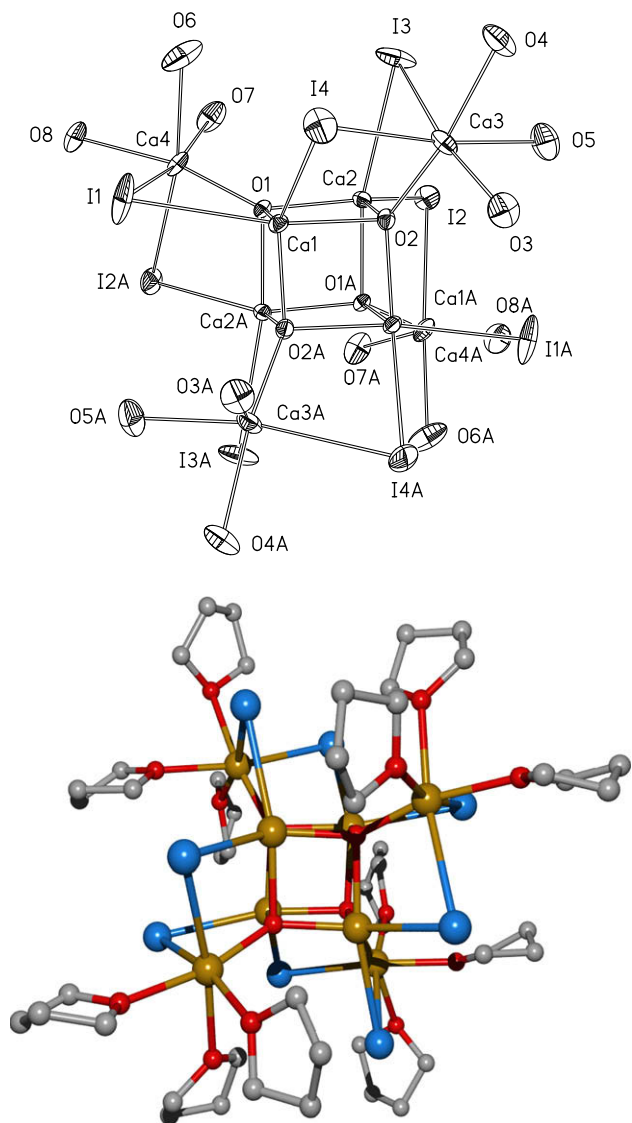**Fig. 1.** Perspective drawing and numbering scheme of $[(CaO)_4 \cdot 4 \, (thf)_3CaI_2]$ (**1**) (color code: C grey, Ca brown, I blue, O red). Symmetry-related atoms ($-x, -y - 1, z$) are marked with an A. The H atoms are omitted for clarity reasons, the disordering of the THF ligands is not shown. Selected bond lengths (Å): Ca1–I1 3.183(3), Ca1–I4 3.199(3), Ca1–O1 2.258(8), Ca1–O2 2.278(8), Ca1–O2A 2.223(9), Ca2–I2 3.181(2), Ca2–I3 3.184(2), Ca2–O1 2.231(8), Ca2–O1A 2.292(8), Ca2–O2 2.248(8), Ca3–I3 3.232(3), Ca3–I4 3.194(3), Ca3–O2 2.158(8), Ca3–O3 2.37(1), Ca3–O4 2.44(1), Ca3–O5 2.38(1), Ca4–I1 3.231(3), Ca4–I2A 3.218(3), Ca4–O1 2.158(8), Ca4–O6 2.453(2), Ca4–O7 2.40(1), Ca4–O8 2.42(1).

coordinate calcium atoms Ca1 and Ca2 are in distorted trigonal bipyramidal environments, whereas the outer hexa-coordinate alkaline earth metal atoms are in distorted octahedral coordination spheres. Due to this fact, the iodine–calcium as well as oxide–calcium distances to the inner metal atoms are smaller than to the outer ones. The distances between the calcium atoms (Ca3 and Ca4) and the oxygen atoms of the THF ligands adopt values between 2.37(1) and 2.45(2) Å.

The stability of the cube-like structure of the inner Ca_4O_4 fragment is in agreement with *ab initio* calculation [29]. Other isomers such as eight-membered rings or ladder-like structures are disfavoured. Calculated Mulliken charges of Ca in these calcium oxide compounds lie between +1 and +1.5 suggesting significant covalent contributions to the Ca–O bonds. Therefore it is not surprising

that the Ca_4O_4 heterocubane fragment was already found in other molecules such as $Li[\{Ca_7(\mu_3\text{-}OH)_8I_6(thf)_{12}(\mu\text{-}I)]$ with two heterocubane moieties with a common corner [30]. Due to OH units with reduced anionic charge compared to the oxide anions in **1** larger Ca–O distances with an average value of 2.323(2) Å were observed. The Ca–O_{THF} distances of 2.42(1) Å lie in the same expected range as observed for **1**. Fused heterocubanes with a common face were found in a hexa-nuclear calcium oxide ethoxide, $[Ca_6(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_4(OEt)_4]$ [31].

Molecular structure and numbering scheme of $[\{(thf)Ca(O\text{-}CH{=}CH_2)_2\}_4 \cdot CaO \cdot CaI_2]$ (**2**) are displayed in Fig. 2 omitting the disordering of the vinylalcoholate for clarity reasons. The central unit consists of an oxygen-centered Ca_6 octahedron with two opposite corners binding to iodine atoms. The calcium atoms of other corners are bound to THF molecules. All faces are capped by the oxygen atoms of the vinylalcoholate anions. Thus the hexa-coordinate calcium atoms are in distorted octahedral environments. The Ca···Ca distances vary between 3.271(2) and 3.276(2) Å.

The Ca1–I1 bond length of 306.9(1) Å is slightly smaller than the values observed for ether adducts of CaI_2 such as $[(thf)_4CaI_2]$ (3.106(2) Å [32], 3.1125(9) Å [33]) or for the water complex $[(H_2O)_4CaI_2]$ (3.127(7) Å [34]), larger coordination numbers lead to an enhancement of the Ca–I distances [35]. It is well known that Ca–I bonds cannot be described by ionic interactions alone but exhibit significant covalent contributions (see e.g. the discussion of Hanusa and coworkers [32]). This fact leads to a reduction of the positive charge on Ca1 and hence to slightly larger Ca1–O7 bond lengths of 2.328(1) Å compared to Ca2–O7 (2.304(1) Å) and Ca3–O7 (2.301(1) Å) with calcium atoms bound to THF molecules.

3. Discussion and conclusion

THF solutions of arylcalcium iodide have to be kept below $-30\,°C$ in order to prevent degradation reactions. At higher temperatures ether cleavage reactions occur which lead to a complete decomposition of THF. In Eq. (3) the results obtained thus far are summarized. The initial step is the α-deprotonation followed by a scission of the ether backbone as described earlier for organolithium compounds [36]. Ethene and vinylalcoholate were observed by NMR spectroscopy. During this degradation reaction, however, THF as well as the vinylalcoholate react with still present arylcalcium compound. Deprotonation of vinylalcoholate liberates oxide-containing species besides arene [17] which are trapped by still present phenylcalcium iodide, leading to the formation of oxygen-centered aryl-containing cage compounds such as $[\{(thf)_2\text{-}Ca(Ph)I\}_3 \cdot (thf)CaO]$ (**A**) [13]. However, even though this compound was crystallized it also slowly decomposes in THF. In order to accelerate this degradation reaction, the solution of phenylcalcium iodide in THF was heated under reflux which led to isolation of $[(CaO)_4 \cdot 4 \, (thf)_3CaI_2]$ (**1**) with a yield of 76%. During this procedure the amount of vinylalcoholate anions decreased as described earlier [17]. At elevated temperatures the phenyl groups of starting $[(thf)_4Ca(Ph)I]$ and of cage compound **A** were able to deprotonate THF molecules as well as vinylalcoholate anions leading to the aryl-free cage compound **1**.

Due to the fact that phenylcalcium iodide reacts with THF as well as the vinylalcoholate anion, large concentrations of the vinylalcoholate were not accessible. Therefore, only the rate of the first deprotonation step of THF should be enhanced at low or room temperature in order to minimize the degradation of the vinylate anions. This goal can be achieved *via* addition of diethylzinc and the formation of more reactive calcium diethyldiphenylzincate [24,25]. This zinc-mediated degradation enhances the

rate of α-deprotonation of THF and crystalline [{(thf)Ca(O–CH=CH$_2$)$_2$}$_4$ · CaO · CaI$_2$] (**2**) was obtained with a yield of 48%.

(3)

with mesitylene (1,3,5-trimethylbenzene) as internal standard: ^{1}H NMR (200.13 MHz, 25 °C, [D$_6$]benzene): δ 1.29 (48H, m, CH$_2$
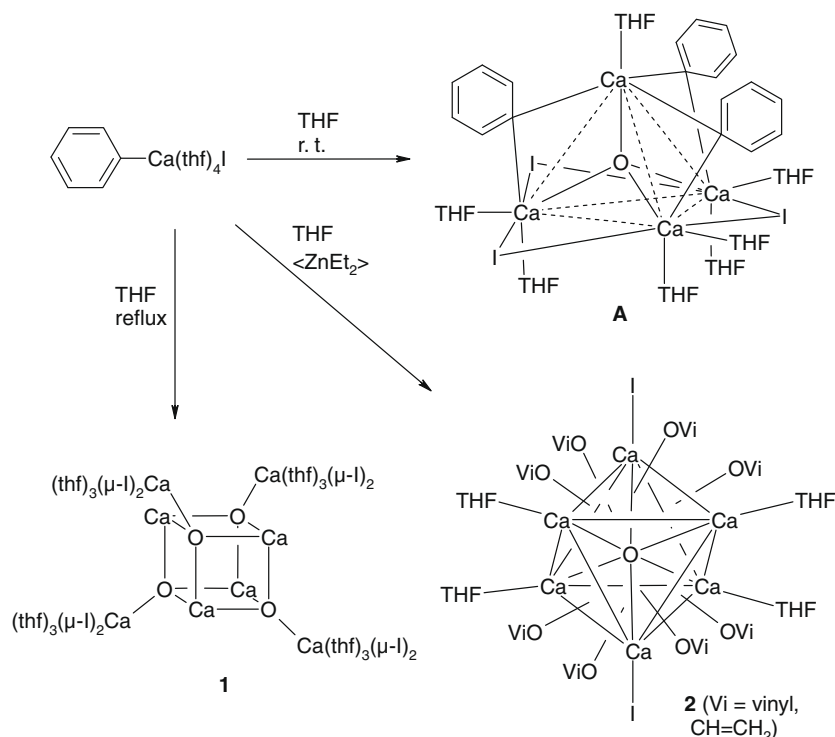
4. Experimental

All manipulations were carried out in an argon atmosphere using standard Schlenk techniques. The solvents were dried according to common procedures and distilled under argon, deuterated solvents were dried, degassed, and saturated with argon. ^{1}H and ^{13}C{^{1}H} spectra were obtained on a Bruker AC 400 MHz spectrometer. IR measurements were carried out using the Perkin–Elmer System 2000 FTIR. Melting and decomposition points were measured with a Reichert-Jung apparatus type 302102 and are uncorrected. ZnEt$_2$ (1 M, hexane solution) was purchased from Alfa Aesar. PhCaI(thf)$_4$ was prepared according to the literature procedure [37].

4.1. Synthesis of [(CaO)$_4$ · 4 (thf)$_3$CaI$_2$] (**1**)

A THF solution of PhCaI(thf)$_4$ (25.0 mL, 0.98 mmol, 0.039 M) was heated under reflux for 2 h and additionally stirred for 12 h at ambient temperature. All volatiles were distilled off (Composition determined via GC–MS measurements: THF and benzene (major part), and biphenyl as minor part) and the pale orange residue was dried in vacuum. Extraction with toluene (2 × 3 mL; 40 °C), filtration and storage at 4 °C affords 0.21 g of colorless, highly refracting crystals of **1** (93 μmol, 76%) during 1 week.

Physical data for **1**. Dec. above 113 °C (brownish clouding and loss of THF). Anal. Calc. for C$_{48}$H$_{96}$Ca$_8$I$_8$O$_{16}$ (2265.13 g mol^{-1}): Ca, 14.15; I, 44.82. Found: Ca, 14.36; I, 44.32%. NMR measurements

(thf)), 3.48 (48H, m, CH$_2$O (thf)). ^{13}C{^{1}H} NMR (50.33 MHz, 25 °C, [D$_6$]benzene): δ 25.6 (24C, CH$_2$ (thf)), 68.2 (24C, CH$_2$O (thf)). IR (Nujol, KBr, cm^{-1}): 2919 vs (br), 2853 vs, 1602 w, 1460 vs, 1376 s, 1283 m, 1260 m, 1064 m, 1032 s, 886 w, 875 w, 752 w, 721 w, 600 m (br).

4.2. Synthesis of [{(thf)Ca(O–CH=CH$_2$)$_2$}$_4$ · CaO · CaI$_2$] (**2**)

During the synthesis and the complete workup procedure the temperature increased at no point above −10 °C. A THF solution of PhCaI(thf)$_4$ (30.0 mL, 6.78 mmol, 0.226 M) was cooled to −25 °C and ZnEt$_2$ (3.39 mL, 3.39 mmol, 1 M) in hexane was added drop wise. Then stirring was continued at this temperature for 12 additional hours, affording a microcrystalline colorless solid. Separation of the solid (1.85 g) and characterization via NMR measurements and metal analysis (Ca, Zn) suggested a formula of [(thf)$_6$Ca][ZnEt$_2$Ph$_2$] (2.46 mmol, 73% referring to ZnEt$_2$ and 36% referring to PhCaI(thf)$_4$) [38]. The mother liquor was concentrated to dryness and the resulting pale yellow residue was extracted three times with 4 mL of toluene at −15 °C. The combined extracts were reduced to 4 mL, filtration and storage over 45 days at −20 °C led to crystallization of 0.62 g of colorless crystals (0.54 mmol, 48% referring to PhCa(thf)$_4$I) of **2** with an icosahedral shape.

Physical data for **2**. Dec. above 56 °C (clouding). Anal. Calc. for C$_{32}$H$_{56}$Ca$_6$I$_2$O$_{13}$ (1143.06 g mol^{-1}): Ca, 21.04; I, 22.20. Found: Ca, 21.21; I, 21.98%. ^{1}H NMR (400.25 MHz, 25 °C, [D$_8$]THF): δ 1.73

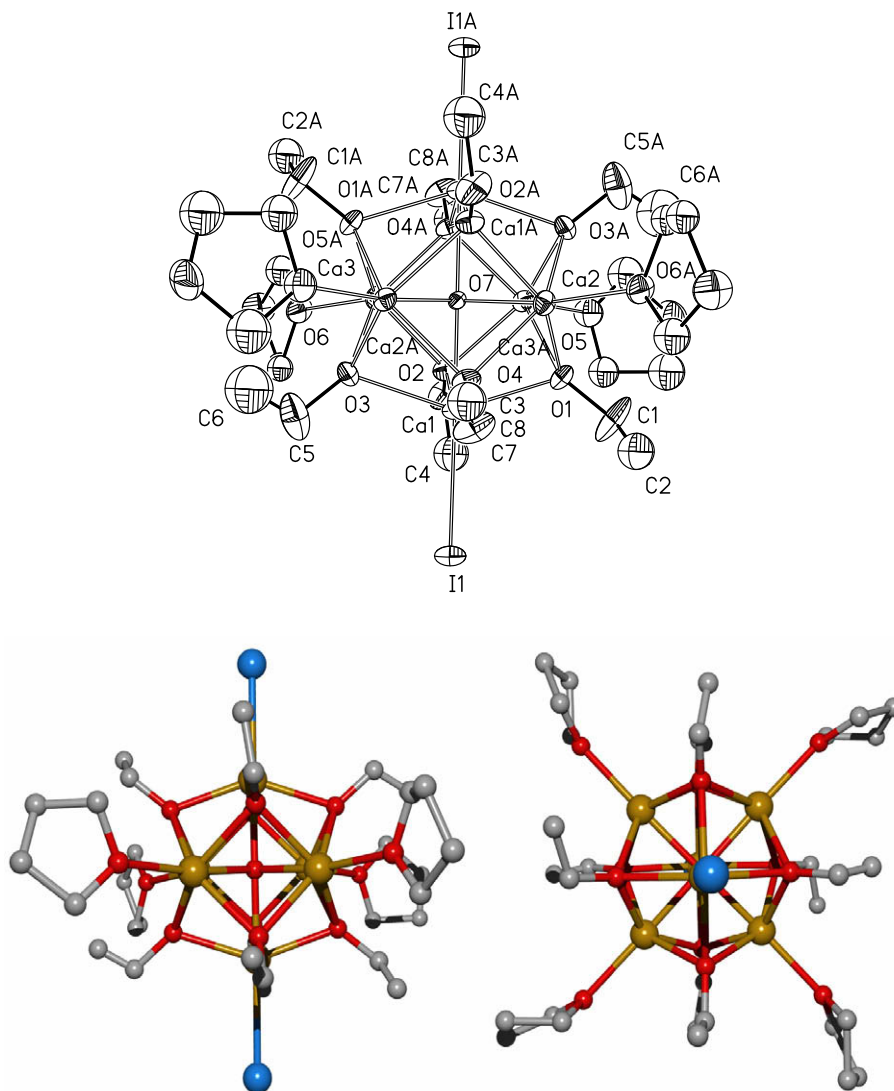**Fig. 2.** Molecular structure of [{(thf)Ca(O–CH=CH₂)₂}₄ · CaO · CaI₂] (**2**) (color code: C grey, Ca brown, I blue, O red). Symmetry-related atoms ($-x + 2$, $-y + 1$, $-z + 1$) are marked with an A. The H atoms are neglected for clarity reasons, the disordering of the vinyl groups is not shown. The upper picture shows the numbering scheme, the bottom figures give the side view of **2** and the view along the I1–C1–O7 axis. Selected bond lengths (Å): Ca1–I1 3.069(1), Ca1–O1 2.389(5), Ca1–O2 2.391(5), Ca1–O3 2.389(5), Ca1–O4 2.400(5), Ca1–O7 2.328(1), Ca2–O1 2.368(5), Ca2–O2 2.363(5), Ca2–O3A 2.371(5), Ca2–O4A 2.364(5), Ca2–O5 2.394(6), Ca2–O7 2.304(1), Ca3–O1A 2.363(5), Ca3–O2 2.374(5), Ca3–O3 2.372(5), Ca3–O4A 2.367(5), Ca3–O6 2.392(5), Ca3–O7 2.301(1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(m, CH_2 (thf)), 3.59 (m, CH_2O (thf)), 3.39 (8H, d, J_C = 6.2 Hz, OCH=CH_2), 3.83 (8H, d, J_t = 13.9 Hz, OCH=CH_2), 6.15 (8H, dd, J_C = 6.2 Hz, J_t = 14.0 Hz, OCH=CH_2). ^{13}C{^{1}H} NMR (100.65 MHz, 25 °C, [D$_8$]THF): δ 25.3 (CH_2 (thf)), 67.34 (CH_2O (thf)), 68.7 (8C, OCH=CH_2), 68.7 (8C, OCH=CH_2). IR (Nujol, KBr, cm^{-1}): 3445 m, 3176 w, 2923 vs, 2722 s, 2669 m, 1716 w, 1615 m, 1558 w, 1460 vs, 1377 vs, 1305 m, 1154 m, 1112 m, 1073 m, 1035 s, 1028 m, 973 m, 963 s, 917 m, 887 s, 722 s, 667 w, 498 w.

Crystal structure determinations of **1** and **2**. The intensity data for the compounds **1** and **2** were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects [39,40]. The structures were solved by direct methods (SHELXS) [41] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97) (Table 1) [42]. All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered non-hydrogen atoms were refined aniso-

tropically [42]. XP (SIEMENS Analytical X-ray Instruments Inc.) was used for structure representations.

5. Supplementary material

CCDC 709990 and 709991 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.

Table 1
Crystal data and refinement details for the X-ray structure determinations of **1** and **2**.

Compound	**1**	**2**
Formula	$C_{48}H_{96}Ca_8 I_8O_{16}$	$C_{32}H_{56}Ca_6 I_2O_{13}$
Formula weight (g mol^{-1})	2265.09	1143.05
T (°C)	−90(2)	−90(2)
Crystal system	Orthorhombic	Tetragonal
Space group	$P2_12_12$	$P4_2/n$
a (Å)	14.6135(3)	17.9545(8)
b (Å)	21.4643(3)	17.9545(8)
c (Å)	13.6582(3)	16.1627(7)
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	90.00	90.00
V (Å^3)	4284.15(14)	5210.3(4)
Z	2	4
ρ (g cm^{-3})	1.756	1.457
μ (cm^{-1})	34.21	18.44
Measured data	37 707	35 943
Data with $I > 2\sigma(I)$	8319	3239
Unique data/R_{int}	9792/0.1066	5962/0.0692
wR_2 (all data, on F^2)[a]	0.2485	0.1958
R_1 $(I > 2\sigma(I))$[a]	0.0908	0.0657
s[b]	1.132	1.022
Residual density (e Å^{-3})	1.481/−2.187	1.229/−0.675
Flack-parameter	0.07(7)	–
Absorption method	None	None
CCDC No.	709991	709990

[a] Definition of the R indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.

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

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