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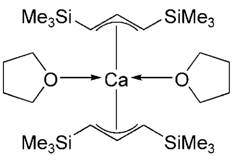
Organocalcium Chemistry

Bis(allyl)calcium**

Phillip Jochmann, Thomas S. Dols, Thomas P. Spaniol, Lionel Perrin, Laurent Maron,* and Jun Okuda*

In contrast to the widely employed organomagnesium and organolithium compounds,[1,2] the σ and π complexes of the heavier alkaline earth metals calcium, strontium, and barium[3] have not achieved their full potential. Whereas the chemistry of cyclopentadienyl (Cp) calcium compounds is fairly well developed, that of Cp-free alkyl,[4] alkynyl,[5] aryl,[6] benzyl,[7] indenyl,[8] and fluorenyl[9] calcium compounds has just begun unfolding. Allyl calcium compounds of unknown structure were first mentioned in a patent as polymerization initiators for vinylic monomers.[10] The first structurally characterized calcium–allyl bond was reported by Hanusa et al. for $[Ca\{\eta^3\text{-}C_3(SiMe_3)_2H_3\}_2(thf)_2]$ (**1**), the reactivity of which is suppressed by bulky ligands and stabilization through negative hyperconjugation of the silyl moieties.[11]



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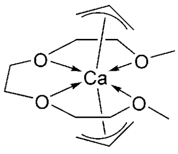

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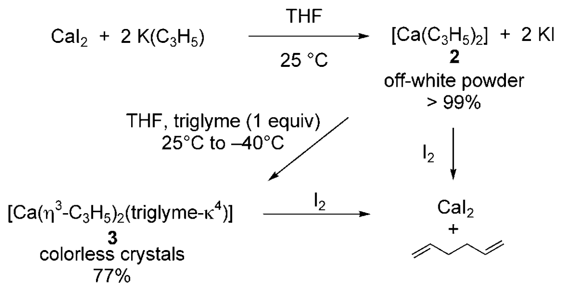
Herein we report the synthesis of the unexpectedly soluble parent bis(allyl)calcium complex, the crystal structure of a Lewis base adduct, and preliminary reactivity studies.



Scheme 1. Synthesis of bis(allyl)calcium **2**, its triglyme adduct **3**,and formation of 1,5-hexadiene upon addition of I_2 to **2** and **3**.

Bis(allyl)calcium $[Ca(C_3H_5)_2]$ (**2**) was obtained in quantitative yield by salt metathesis of anhydrous CaI_2 with two equivalents of $K(C_3H_5)$ (Scheme 1). The non-pyrophoric, off-white product is highly soluble in THF and pyridine; use of the latter solvent leads to decomposition over a period of days. Compound **2** is insoluble in hydrocarbons, which is most likely due to its presumably polymeric nature. Addition of one equivalent of triglyme to a THF solution of **2** (Scheme 1) provided block-like single crystals of the triglyme adduct **3**, which were suitable for X-ray analysis. The ^1H NMR spectrum of **2** (Figure 1) in $[D_8]$THF at room temperature has a doublet at $\delta = 2.32$ ($^3J(H,H) = 12.0$ Hz) and a quintet at $\delta = 6.28$ ($^3J(H,H) = 12.0$ Hz), which are ascribed to the terminal methylene protons and to the internal methine proton of the allyl groups.

The observed coupling constant $^1J(C,H)$ for the terminal allylic carbon atoms is 147.8 Hz. This value is similar to C,H coupling constants reported for allyllithium ($^1J(C,H) = 146.5$ Hz) and allylsodium ($^1J(C,H) = 149.5$ Hz), but larger

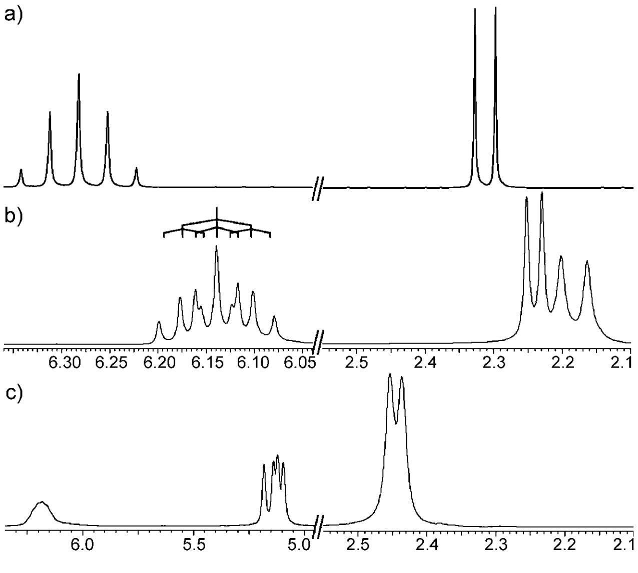


Figure 1. ^1H NMR spectra of **2** in a) $[D_8]$THF at 25 °C, b) −80 °C, and c) 25 °C in $[D_5]$pyridine. Scale under spectrum (b) also pertains to (a).

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[*] Dr. L. Perrin, Prof. Dr. L. Maron
Université de Toulouse et CNRS
INSA, UPS, CNRS; UMR 5215 LPCNO
135 avenue de Rangueil, 31077 Toulouse (France)
Fax: (+33)5-6155-9697
E-mail: laurent.maron@irsamc.ups-tlse.fr
P. Jochmann, T. S. Dols, Dr. T. P. Spaniol, Prof. Dr. J. Okuda
Institute of Inorganic Chemistry, RWTH Aachen University
Landoltweg 1, 52056 Aachen (Germany)
Fax: (+49) 241-809-2644
E-mail: jun.okuda@ac.rwth-aachen.de

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than the value for allylmagnesium bromide (${}^1J$(C,H) = 135.5 Hz), indicating a greater contribution of s orbitals.[12] Heating a solution of **2** in [D$_8$]THF to 60 °C for 4 h did not result in any decomposition. After the temperature is decreased to −80 °C, the doublet splits into two doublets of different coupling constants and the quintet into a triplet of triplets (Figure 1). This observation implies the inequivalence of the terminal *cis* and *trans* protons at lower temperatures. As the η^3-bonding mode is the only one observed even at −80 °C, the π-σ-π rearrangement of the allyl ligands proceeds with an extremely low activation energy or does not occur.[13a] The ^{1}H NMR spectrum of **3** in [D$_8$]THF at room temperature corresponds to the signals for **2** and for free triglyme. However, in [D$_5$]pyridine an η^1 bonding mode is observed, which is clearly indicated by the presence of three doublets at $\delta = 2.45$ (${}^3J$(H,H) = 7.0 Hz), 5.11 (${}^3J$(H,H) = 10.3 Hz), and 5.16 ppm (${}^3J$(H,H) = 17.6 Hz) and a broad signal at $\delta = 6.18$ ppm in the ^{1}H NMR spectrum. These resonances are assigned to the metal-bound methylene protons, the terminal *cis* and *trans* protons and the methine proton, respectively.

The solid state structure of the adduct **3** (Figure 2)[14] shows a coordination geometry derived from a pentagonal bipyramid with a vacant site in the equatorial plane. The other four equatorial positions are occupied by the oxygen atoms, and the allyl ligands occupy the apical positions in a *trans* arrangement. The allyl ligands can be regarded as being coordinated to the metal center in an η^3-fashion. The central carbon atom of one allyl ligand (C5) is refined with two split positions without any restraints. The angles C2-Ca-C5A of 149.86(6) Å and C2-Ca-C5B of 146.64(10) Å deviate from linearity.[13b] The C−C bonds within the nondisordered allyl ligand are 1.3886(18) Å for C1–C2 and 1.369(2) Å for C2–C3, indicating charge delocalization, as was reported for **1**.[11] The average Ca−C bond length is 2.72 Å (including the positions for the disordered moiety), and the angle C1-C2-C3 is 129.10(14)°. Similar bond parameters have been reported for allyl complexes of the alkali metals.[15] In contrast, the allyl group is η^1-bonded in allylmagnesium chloride.[16] The metal-to-ligand distance in **3** is slightly larger than in **1**, and about the same as the value documented for the distance between the η^5-Cp rings and the calcium ion in CaCp$_2$ (average 2.80 Å).[17] The average Ca−O bond length is 2.48 Å, which is somewhat larger than the observed C-O distance in **1** (2.353(2) Å).[11]

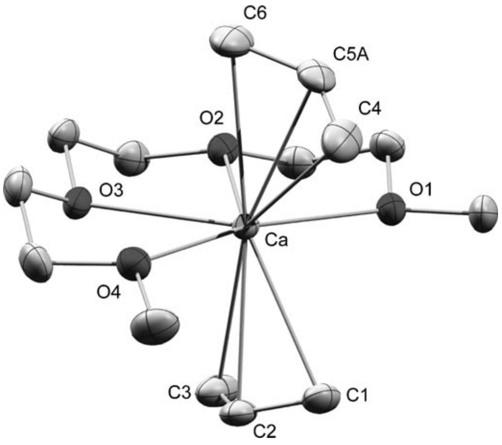


Figure 2. Molecular structure of the triglyme adduct **3**. Only one of the split positions C5A/C5B is shown. Ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ca–C1 2.7127(13), Ca–C2 2.6708(12), Ca–C3 2.8459(14), C1–C2 1.3886(18), C2–C3 1.369(2), Ca–O1 2.4744(9); C1-C2-C3 129.10(14), O1-Ca-O4 162.85(3).

Reaction of compound **2** with I$_2$ resulted in quantitative formation of 1,5-hexadiene (verified by NMR and GC/MS) with concomitant precipitation of CaI$_2$. The analogous reaction using complex **3** showed the same results, except that the precipitation of the calcium salt was prevented by the formation of [CaI$_2$(triglyme-κ^4)$_n$([D$_8$]thf)$_m$]$_k$. Whereas allyl coupling reactions involving nickel complexes are well-known[18] and have been used for preparation of cyclo-olefins,[19] catalytic C−C bond formation involving β-diketiminato calcium acetylides was reported only recently.[20] Whereas oxidative coupling reactions of η^1-allyl and η^1-propargyl ligands have been observed for example for half-sandwich complexes of iron(II) and molybdenum(III), and presumably proceed via intramolecular radical recombination,[21] such oxidative C−C coupling reactions have not been reported for d^0 metal centers.

The reaction of **2** with carbon dioxide resulted in the rapid formation of the insertion product calcium but-3-enoate. This result illustrates the expected high reactivity towards electrophilic substrates such as CO$_2$.

Preliminary investigations into the 1,3-butadiene polymerization in THF using compound **2** (molar ratio monomer/**2** = 100) resulted in quantitative conversion of the monomer, giving polybutadiene with a molecular weight of $M_w = 6.6 \times 10^3$ g mol^{-1} and a narrow molecular weight distribution $M_w/M_n = 1.15$. The 1,2-polybutadiene/1,4-polybutadiene and 1,4-*cis*-polybutadiene/1,4-*trans*-polybutadiene ratios are 0.92 and 0.81, respectively.[22]

The structure and reactivity of complexes **2** and **3** were investigated at the DFT level (B3PW91/SDD for I/6-311++G(d,p) for Ca/6-31G(d,p) for C,H,O, and N).[23] The good agreement between the X-ray crystal structure of **3** and its optimized geometry (Table 1) reveals the adequacy of the

Table 1: Main geometrical parameters and NBO charges for the calculated structure of [Ca(η^3-C$_3$H$_5$)$_2$(triglyme)].

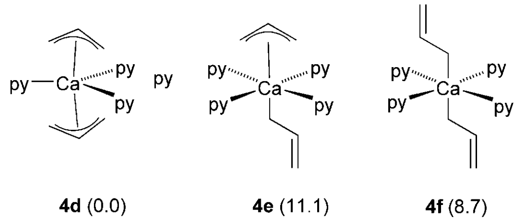
	X-ray	DFT	NBO charges[a]
Ca	–	–	+1.71
Ca–*O1*	2.4744(9)	2.569	−0.62
Ca–*O2*	2.4786(9)	2.601	−0.62
Ca–*O3*	2.5037(9)	2.607	−0.62
Ca–*O4*	2.4684(9)	2.569	−0.62
Ca–*C1*	2.7127(13)	2.694	−0.85
Ca–*C2*	2.6708(12)	2.663	−0.29
Ca–*C3*	2.8459(14)	2.747	−0.83
Ca–*C4*	2.7391(15)	2.689	−0.84
Ca–*C5A*	2.6385(19)	2.666	−0.29
Ca–*C6*	2.7521(14)	2.756	−0.85
O1-Ca-O4	162.85(3)	167.90	–
O2-Ca-O3	66.26(3)	65.38	–
C3-Ca-C6	158.30(5)	160.42	–
C1-Ca-C4	94.77(5)	90.25	–

[a] NBO charges are of atoms in italics.

level of theory used for the coordination properties of calcium. NBO charges of almost +2 and −1 were computed for calcium and each allyl ligand, indicating a highly ionic character of the calcium ligand bond in **3**. The allyl moiety accumulates electron density on its terminal atoms rather than on the central carbon. This is in agreement with its orbital analytical expression.

The fluxional character of **2** including its first solvation sphere was studied. In the presence of up to three THF molecules or one triglyme molecule, no minimum corresponding to σ allyl could be optimized, which suggests the absence of fluctuation of the allyl ligands rather than a fast π–σ–π haptotropic shift. Similarly, no σ allyl complex could be optimized for up to three pyridine molecules coordinated at the metal center.

Optimization of the tetra(pyridine) adduct reveals distinct bonding modes of both pyridine and allyl ligands. Geometry optimization of $[Ca(\eta^3\text{-}C_3H_5)_2(py)_4]$, in which four pyridines lie in a plane, leads to expulsion of one pyridine molecule from the first coordination sphere, and a structure similar to $[Ca(\eta^3\text{-}C_3H_5)_2(py)_3]$ is obtained. In this trigonal bipyramidal complex, the average Ca−C distance is 2.78 Å and a tilt between the equatorial allyl ligands occurs (C2-Ca-C5 143.6°). The *ortho* C−H bonds of the two apical pyridine ligands constrain the allyl ligands in the apical plane of the complex, resulting in a shortening of the distance between the allyl terminal carbon atoms (C3⋯C4 = 3.81 Å). Therefore, a haptotropic shift from π to σ of one or two allyl ligands is required to maintain the coordination of four pyridine ligands. Whereas the optimized symmetric complex $[Ca(\sigma\text{-}C_3H_5)_2(py)_4]$ (**4f**) is 8.7 kcal mol^{-1} less stable than $[Ca(\eta^3\text{-}C_3H_5)_2(py)_3](py)$ (**4d**), the "mixed hapticity" complex $[Ca(\eta^3\text{-}C_3H_5)(\sigma\text{-}C_3H_5)(py)_4]$ (**4e**) is destabilized by 11.1 kcal mol^{-1} (Scheme 2). Although thermodynamically unfavorable, the existence of isomers **4e** and **4f** suggests an equilibrium between $[Ca(\eta^3\text{-}C_3H_5)_2(py)_3](py)$ and $[Ca(\sigma\text{-}C_3H_5)_2(py)_4]$, with a preference for the bis(η^3) complex. $[Ca(\eta^3\text{-}C_3H_5)(\sigma\text{-}C_3H_5)(py)_4]$ (**4e**) may be an intermediate complex in the global haptotropic shift. This result is in agreement with the NMR data of **2** recorded in [D$_5$]pyridine (Figure 1).



4d (0.0) **4e** (11.1) **4f** (8.7)

Scheme 2. Structure and relative free enthalpy (in brackets; kcal mol^{-1}) for the $[Ca(C_3H_5)_2(py)_4]$ isomers. py = pyridine.

Two distinct scenarios were calculated for the mechanism of allyl homocoupling of $[Ca(\eta^3\text{-}C_3H_5)_2(thf)_n]$ induced by I_2. For a concerted cleavage of I_2 and allyl homocoupling, no first- or second-order transition state could be optimized. The reaction thus proceeds via at least two successive steps, which correspond to an electrophilic addition of I_2 to one of the two allyl groups followed by an intramolecular nucleophilic substitution (Figure 3).

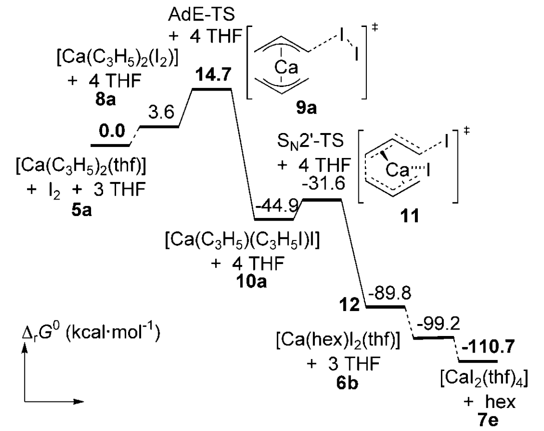


Figure 3. Free-enthalpy profile for the iodine-induced two-step allyl ligand coupling in $[Ca(C_3H_5)_2(thf)_n]$. AdE = electrophilic addition, TS = transition state, hex = 1,5-hexadiene.

For the initial bis(allyl) complex, the intermediate 1,5-hexadiene adduct $[Ca(C_6H_{10})(I)_2]$, and the final calcium salt CaI_2, the optimal first solvation sphere structures were determined (see the Supporting Information) and consequently used in the energy profile.

The electrophilic addition reaction is initiated by the formation of an I_2 adduct on the *exo* face of one allyl ligand. The formation of this adduct is almost thermoneutral (+3.6 kcal mol^{-1}). The activation barrier of the addition is rather low in energy (+14.7 kcal mol^{-1}). The transition state produces the allyl iodide complex $[Ca(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_5I)(I)]$ with a favorable thermodynamic balance of −44.9 kcal mol^{-1}. The second allyl ligand subsequently reacts with allyl iodide in an S_N2' fashion, with an overall energy gain of −31.6 kcal mol^{-1}. The coupling reaction produces the 1,5-hexadiene adduct of CaI_2, which releases the diene to form solvated CaI_2, with a global exergonicity of −110.7 kcal mol^{-1}. It is noteworthy that the replacement of one allyl group by one iodide stabilizes the complex by 45 kcal mol^{-1}. This energy profile demonstrates the thermodynamic feasibility of this reaction, which proceeds with a small activation barrier.

In summary, we have isolated the unexpectedly stable and soluble compound bis(allyl)calcium **2** and determined the solid-state structure of its triglyme adduct **3**. We have also carried out the reaction with I_2 to form 1,5-hexadiene by allyl coupling. DFT-level calculations on solid-state and solution structures are in excellent agreement with experimental results. Preliminary reactivity studies hint at tractable reactivity of **2** and **3** despite their highly basic character.

Experimental Section

$[Ca(C_3H_5)_2]$ (**2**): Allylpotassium (859 mg, 10.7 mmol, 2.1 equiv) was added to a suspension of anhydrous calcium iodide (1.50 g, 5.10 mmol) in THF (50 mL). Potassium iodide precipitated and was filtered off, and the solvent was removed under reduced pressure. After washing with pentane and drying in vacuo, **2** was obtained as an off-white, analytically pure powder. Yield: 622 mg (5.09 mmol, 100 %). Recrystallization from THF gave crystals that melt below room temperature. Elemental analysis (%) calcd for $\mathrm{C_6H_{10}Ca}$ (122.22): C 58.96, H 8.25; found: C 57.99, H 8.95. Low C,H values have frequently been observed for alkaline earth metal compounds.[24] ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): $\delta = 2.32$ (d, $^3J(\mathrm{H,H}) = 12.0$ Hz, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CHC}\mathit{H}_2$), 6.28 ppm (quintet, $^3J(\mathrm{H,H}) = 12.0$ Hz, 2H, $\mathrm{CH_2C}\mathit{H}\mathrm{CH_2}$). ^{13}C NMR (100 MHz, [D$_8$]THF, 25 °C): $\delta = 57.74$ (tt, $^1J(\mathrm{C,H}) = 147.8$ Hz, $^3J(\mathrm{C,H}) = 7.3$ Hz, $\mathit{C}\mathrm{H_2CH}\mathit{C}\mathrm{H_2}$), 147.52 ppm (d, $^3J(\mathrm{C,H}) = 7.3$ Hz, $\mathrm{CH_2}\mathit{C}\mathrm{HCH_2}$). ^{1}H NMR (400 MHz, [D$_8$]THF, −80 °C): $\delta = 2.19$ (d, $^3J(\mathrm{H,H}) = 15.1$ Hz, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CHC}\mathit{H}_2^{trans}$), 2.25 (d, $^3J(\mathrm{H,H}) = 9.0$ Hz, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CHC}\mathit{H}_2^{cis}$), 6.14 ppm (tt, $^3J(\mathrm{H,H}) = 8.8$ Hz, $^3J(\mathrm{H,H}) = 15.3$ Hz, 2H, $\mathrm{CH_2C}\mathit{H}\mathrm{CH_2}$). ^{1}H NMR (400 MHz, [D$_5$]pyridine, 25 °C): $\delta = 2.45$ (d, $^3J(\mathrm{H,H}) = 7.0$ Hz, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH{=}CH_2}$), 5.11 (d, $^3J(\mathrm{H,H}) = 10.3$ Hz, 2H, $\mathrm{CH_2CH{=}C}\mathit{H}_2^{cis}$), 5.16 (d, $^3J(\mathrm{H,H}) = 17.6$ Hz, 2H, $\mathrm{CH_2CH{=}C}\mathit{H}_2^{trans}$), 6.18 ppm (br, 2H, $\mathrm{CH_2C}\mathit{H}\mathrm{{=}CH_2}$). ^{13}C{^{1}H} NMR (100 MHz, [D$_5$]pyridine, 25 °C): $\delta = 50.17$ ($\mathit{C}\mathrm{H_2CH{=}CH_2}$), 114.50 ($\mathrm{CH_2}\mathit{C}\mathrm{H{=}CH_2}$), 138.76 ppm ($\mathrm{CH_2CH{=}}\mathit{C}\mathrm{H_2}$).

[Ca(η^3-$\mathrm{C_3H_5}$)$_2$(triglyme-κ^4)] (**3**): A solution of triglyme (87 mg, 0.49 mmol, 1.0 equiv) in THF (0.5 mL) was added to a solution of **2** (60 mg, 0.49 mmol) in THF (2.0 mL). Cooling gave colorless block-like crystals that were suitable for X-ray analysis. Yield 114 mg (0.38 mmol, 77 %). ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): $\delta = 2.28$ (d, $^3J(\mathrm{H,H}) = 12.0$ Hz, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CHC}\mathit{H}_2$), 3.43 (s, 6H, $(\mathrm{C}\mathit{H}_3\mathrm{OCH_2CH_2OCH_2})_2$), 3.57 (m, 4H, $(\mathrm{CH_3OC}\mathit{H}_2\mathrm{CH_2OCH_2})_2$), 3.63 (m, 8H, $(\mathrm{CH_3OCH_2C}\mathit{H}_2\mathrm{OC}\mathit{H}_2)_2$), 6.19 ppm (quintet, $^3J(\mathrm{H,H}) = 12.0$ Hz, 2H, $\mathrm{CH_2C}\mathit{H}\mathrm{CH_2}$). ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]THF, 25 °C): $\delta = 57.02$ ($\mathit{C}\mathrm{H_2CH}\mathit{C}\mathrm{H_2}$), 59.83 ($(\mathit{C}\mathrm{H_3OCH_2CH_2OCH_2})_2$), 70.94 ($(\mathrm{CH_3OCH_2CH_2O}\mathit{C}\mathrm{H_2})_2$), 71.22 ($(\mathrm{CH_3OCH_2}\mathit{C}\mathrm{H_2OCH_2})_2$), 72.44 ($(\mathrm{CH_3O}\mathit{C}\mathrm{H_2CH_2OCH_2})_2$), 147.61 ppm ($\mathrm{CH_2}\mathit{C}\mathrm{HCH_2}$). ^{1}H NMR (400 MHz, [D$_8$]THF, −80 °C): $\delta = 2.22$ (br d, $^3J(\mathrm{H,H}) = 10.0$ Hz, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CHC}\mathit{H}_2$), 3.54 (s, 6H, $(\mathrm{C}\mathit{H}_3\mathrm{OCH_2CH_2OCH_2})_2$), 3.69 (br s, 4H, $(\mathrm{CH_3OC}\mathit{H}_2\mathrm{CH_2OCH_2})_2$), 3.73 (br s, 8H, $(\mathrm{CH_3OCH_2C}\mathit{H}_2\mathrm{OC}\mathit{H}_2)_2$), 6.02 ppm (tt, $^3J(\mathrm{H,H}) = 9.7$ Hz, $^3J(\mathrm{H,H}) = 15.2$ Hz, 2H, $\mathrm{CH_2C}\mathit{H}\mathrm{CH_2}$).

Polymerization of 1,3-butadiene: Compound **2** (15 mg, 0.12 mmol) was added to a solution of 1,3-butadiene (6.5 wt %, 10.0 g, 12.0 mmol) in THF. After stirring for 20 h at 45 °C, the reaction was quenched by addition of 1.0 mL of *i*PrOH. Pouring the reaction mixture into 100 mL of cold methanol with a small amount of 2,6-di-*tert*-butylphenol led to the precipitation of polybutadiene. Yield: 0.65 g (100 %). The determination of 1,2-polybutadiene/1,4-polybutadiene and 1,4-*cis*-polybutadiene/1,4-*trans*-polybutadiene ratios was performed as described previously.[25]

Reaction of **2** with $\mathrm{CO_2}$: Compound **2** (30 mg, 0.25 mmol) was dissolved in [D$_8$]THF (0.6 mL) and exposed to 1 bar $\mathrm{CO_2}$. A precipitate immediately formed, and the $\mathrm{CO_2}$ supply was then stopped. After filtration, the ^{1}H NMR spectrum showed signals for unreacted **2** and the product, calcium but-3-enoate.[26] Further exposure to $\mathrm{CO_2}$ resulted in complete solidification of the reaction mixture.

Reaction of **2** or **3** with $\mathrm{I_2}$: Iodine (26 mg, 0.10 mmol, 0.5 equiv) was added to a solution of **2** (25 mg, 0.21 mmol) in [D$_8$]THF (0.5 mL). The colorless precipitate of $\mathrm{CaI_2}$ was removed. The ^{1}H NMR spectrum showed resonances for 1,5-hexadiene and **2** in a molar ratio of 1/1. Further addition of $\mathrm{I_2}$ (26 mg, 0.10 mmol, 0.5 equiv) resulted in complete conversion into 1,5-hexadiene (99% by NMR and GC/MS) and precipitation of $\mathrm{CaI_2}$. Analogous reaction using **3** led to a quantitative conversion into 1,5-hexadiene. The precipitate was identified as $\mathrm{CaI_2}$ by precipitation of iodide as AgI and oxidation to $\mathrm{I_2}$ by chlorine.

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[14] Crystal data for complex **3**: $\mathrm{C_{14}H_{28}CaO_4}$, $M_r = 300.44$, $T = 130$ K, crystal size $0.21 \times 0.26 \times 0.27$ mm^3, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 0.382$ mm^{-1}; monoclinic, $P2_1/n$, $a = 8.4399(4)$ Å, $b = 22.9328(11)$ Å, $c = 9.0724(4)$ Å, $\beta = 107.8020(10)°$, $V = 1671.89(13)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.194$ Mg m^{-3}, $2\theta_{\max} = 61.8°$, 24991 reflections collected, 4953 independent ($R_{\mathrm{int}} = 0.0356$), final $R1 = 0.0357$, $wR2 = 0.0944$ ($I > 2\sigma(I)$), GoF = 1.040, $\rho_{\max} = 0.381$ e Å^{-3}, $\rho_{\min} = -0.483$ e Å^{-3}. CCDC 721251 contains 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.

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