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The Allylcalcium Monocation: A Bridging Allyl Ligand with a Non-Bent Coordination Geometry**

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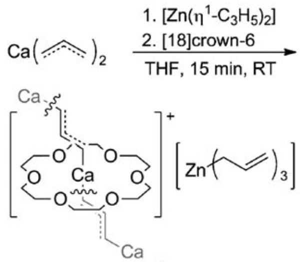
In memory of Kurt Dehnicke

The study of the allyl ligand at s block metal centers is of interest in the context of understanding the nature of the interaction between the simplest delocalized π system with an electropositive metal.[1] Recently, research in this field has focused on alkaline earth metal complexes. For beryllium and magnesium, the η^1 binding mode with a σ-type metal–carbon bond is favored.[1e,2] Theoretical studies suggest that allylberyllium compounds could form an η^3 binding mode in the absence of coordinating solvents.[2a,3] Experimental evidence of π-type metal–ligand interactions for an allyl magnesium compound in the absence of coordinating solvents has recently been reported by Hanusa et al.[4] In all allyl compounds of the heavier homologues calcium, strontium, and barium isolated to date, the allyl moiety invariably adopts an η^3 binding mode.[1e,5]

Monocationic organometallic derivatives of Ca, Sr, and Ba[6] could exhibit a reactivity pattern different from that of their neutral counterparts, as was found for Group 3, 4, and 13 metals.[7] However, the isolation and characterization of monocationic organocalcium compounds is extremely difficult owing to fast Schlenk equilibria.[6,8] Only one compound of this type has been fully characterized so far using the $(C_5Me_5)^-$ ligand.[9] Herein we present the isolation and structural characterization of the allylcalcium monocation, a rare example of a cationic organocalcium compound.

Reactions of bis(allyl)calcium with weak Brønsted acids, such as $[NEt_3H][BPh_4]$, or Lewis acids, such as BPh_3 or $Al(CH_2SiMe_3)_3$, led to the formation of monoionic complexes in solution, as determined by ^{1}H NMR spectroscopy. However, only salt-like compounds containing a calcium dication were obtained upon crystallization, even in the presence of neutral chelating ligands $[Ca([18]crown\text{-}6)(thf)_2][\{B(C_6H_5)_3(\eta^1\text{-}C_3H_5)\}_2]$ or $[Ca(thf)_6][\{Al(CH_2SiMe_3)_3(\eta^1\text{-}C_3H_5)\}_2]$ (see the Supporting Information). Reaction of bis(allyl)calcium with bis(allyl)zinc, followed by the addition of [18]crown-6, allowed the isolation of the monocationic compound **1** in 96% yield (Scheme 1).



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Scheme 1. Synthesis of compound **1** containing an allylcalcium monocation; the allyl ligand in the cationic part shows a μ^2-η^1:η^1 binding mode.

The bonding situation in compound **1** in the solid state was unambiguously established by single-crystal X-ray analysis (see Figure 1 for the molecular structure; Figure 2 shows the arrangement in the solid state). The cationic part of **1** forms an infinite chain. No close interactions with the anion are observed. The coordination geometry around the calcium atom is hexagonal-bipyramidal with the allyl ligands in the axial positions. The calcium atoms are linked by allyl ligands in a *trans* μ^2-η^1:η^1 fashion.[10] This is the first example of a heavy alkaline earth allyl complex exhibiting a σ-allyl–metal interaction. Thus, the η^1 binding mode in alkaline earth allyl complexes is apparently not limited to the lighter homologues beryllium and magnesium.

Along the axis of the hexagonal bipyramidal coordination polyhedron, a C1-Ca1-C3′ angle of 178.80(11)° is observed; that is, there is no significant bending of the C-Ca-C unit. Since the discovery of the bent structure for calcocene,[11] the question has arisen as to when organo alkaline earth compounds show a bent or a non-bent structure.[12] Apart from metallocene complexes, only two calcium compounds have been reported that are relevant in this context. Both of them exhibit bent coordination geometries.[13] Thus, compound **1** is an unprecedented example of a non-metallocene organocalcium compound adopting a non-bent coordination geometry. In combination with earlier work,[13] this result provides experimental evidence of low energy differences between bent and linear structures in organocalcium complexes.

The two Ca−C-bond lengths in compound **1** are very similar (2.593(2) and 2.591(2) Å) and considerably shortened compared to the neutral parent compound $[Ca(\eta^3\text{-}C_3H_5)_2\text{-}$

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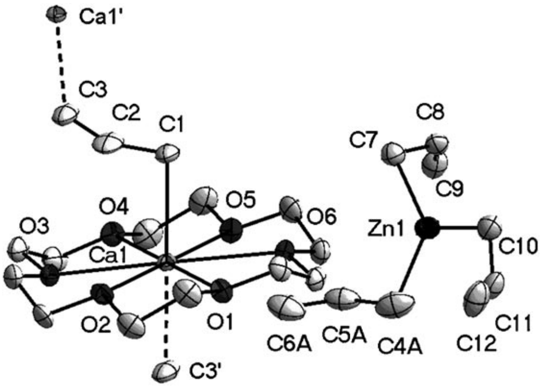

Figure 1. ORTEP representation of the molecular structure of compound **1** (ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity). Carbon atoms C4, C5, and C6 are shown with one split position. Selected bond lengths [Å] and angles [°]: Ca1–C1 2.593(2), Ca1–C3′ 2.591(2), Ca1–O1 2.6863(16), Ca1–O2 2.6623(17), Ca1–O3 2.6438(17), Ca1–O4 2.6756(17), Ca1–O5 2.6332(17), Ca1–O6 2.6644(16), C1–C2 1.321(4), C2–C3 1.357(4), Zn1–C4A 2.02(2), Zn1-C4B 2.083(18), Zn1–C7 2.044(3), Zn1–C10 2.038(3), C4A–C5A 1.48(2), C5A–C6A 1.300(16), C4B–C5B 1.42(3), C5B–C6B 1.350(18), C7–C8 1.460(4), C8–C9 1.325(4), C10–C11 1.467(4), C11–C12 1.327(4); C1-Ca1-C3′ 178.80(11), C1-C2-C3 136.7(4), C4A-C5A-C6A 128.5(14), C4B-C5B-C6B 128.7(14), C7-C8-C9 127.8(3), C10-C11-C12 127.9(3). Primed atoms are related by symmetry code $-x+1.5$, $y+0.5$, z.

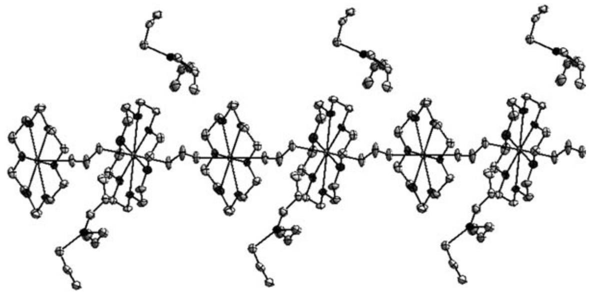

Figure 2. ORTEP representation of the crystal packing in the solid state of **1** (viewed along the *c* axis). To demonstrate the arrangement within the cationic part, six formula units of **1** are shown.

(triglyme)].[5b] The C–C distances in the allyl fragment of the cationic part of **1** are similar to each other and significantly shorter than the corresponding bond lengths in [Ca(η^3-C_3H_5)$_2$(triglyme)].[5b] These effects are ascribed to the increased Lewis acidity of the calcium atoms owing to their formally monocationic character and for the latter case also to the interaction of one allyl ligand with two metal centers. The C-C-C angle in the allyl fragment of the cation has a value of 136.7(4)°, which agrees well with the value calculated for a delocalized allylic π system.[14]

With the allyl ligands being in the axial positions of the hexagonal-bipyramidal coordination polyhedron, the oxygen atoms of the crown ether ligand are consequently located in the equatorial plane (Σ(O1-6-Ca1-O1-6) = 360°). The Ca–O distances range from 2.6332(17) Å to 2.6863(13) Å and compare well to other complexes of calcium with [18]crown-6.[8,15] They are slightly longer than the Ca–O bonds found in calcium complexes with non-macrocyclic ether ligands, which is due to the geometry dictated by the macrocycle.[5b,16]

In the anionic part of **1**, the zinc atom adopts a trigonal-planar coordination geometry, with each of the three allyl ligands coordinating in an η^1 fashion to the metal center. One of these allyl ligands was refined with split positions. In both cases, the angle sum around the metal center is nearly 360°. The Zn–C-bond lengths range from 2.02(2) to 2.083(18) Å. Both parameters agree with results obtained for other tris(organo)zincates.[17] The three allyl ligands of the anion exhibit one long and one short C–C-bond. The distances correspond to a single and a double bond, respectively, in agreement with the η^1 coordination mode. The C-C-C angles have values of 127.8(3) to 128.7(14)° and are significantly smaller than the corresponding angle in the cationic part. This gives further evidence of a low extent of π-electron delocalization in the allyl ligands in $[Zn(C_3H_5)_3]^-$.[14]

Compound **1** is insoluble in aliphatic and aromatic hydrocarbons, poorly soluble in diethyl ether, and very soluble in THF. Upon dissolving compound **1** in THF at room temperature, ligand scrambling is observed, as indicated by the appearance of only one set of signals for the allyl moieties in the ^{1}H NMR spectrum (Figure 3a).[18] The number, chemical shifts, and multiplicities of these resonances are in agreement with an η^3 binding mode, a μ^2-η^1:η^1 binding mode, and/or η^1-bound allyl ligands exchanging fast on the NMR timescale. Variable-temperature (VT) ^{1}H NMR measurements of **1** in [D$_8$]THF reveal a coalescence temperature of −20 °C (Figure 3b). Two sets of well-separated resonances for the allyl moieties, with a relative integral ratio of 1:3, are observed at −80 °C. This result indicates that the ionic structure of **1** is maintained in solution (Figure 3c). At this

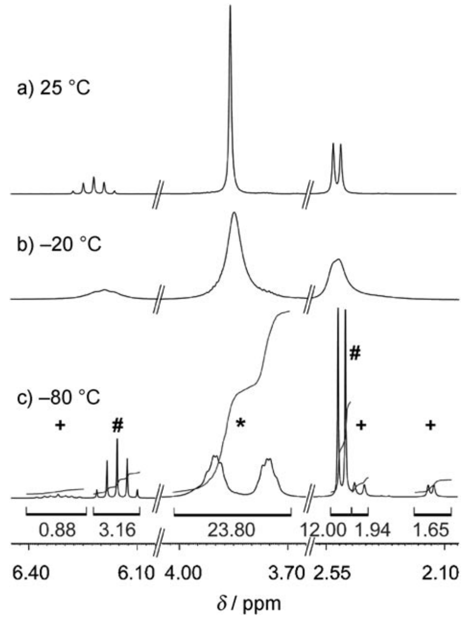

Figure 3. ^{1}H NMR spectra of a solution of **1** in [D$_8$]THF at a) 25 °C, b) −20 °C, and c) −80 °C. The resonances that correspond to the crown ether (*) and the allyl ligands of the calcium monocation (+) and the zincate (#) are indicated.

low temperature, two resonances corresponding to the protons bound to the crown ether appear owing to their diastereotopicity (Figure 3c). The proton-coupled ^{13}C NMR spectrum of **1** at −80 °C reveals an η^3 or a μ^2-η^1:η^1 binding mode for the allyl ligand of the cation (a ddd is observed for the methylene groups). The $^1J_{\mathrm{CH}}$ coupling constants of 142.6 and 153.7 Hz in the allyl ligand of the cation hint at a hybridization between sp^2 and sp^3 for all three carbon atoms, again in agreement with a delocalized π system. In contrast to neutral bis(allyl)zinc, the η^1 binding mode of the allyl moieties in the anion of **1** is not frozen out at temperatures as low as −90 °C.[19]

The exchange of allyl ligands in compound **1** in THF solution was investigated by lineshape analysis. Values of $\Delta G^{\neq} = (50.0 \pm 0.8)\ \mathrm{kJ\,mol^{-1}}$, $\Delta H^{\neq} = (37.1 \pm 0.8)\ \mathrm{kJ\,mol^{-1}}$, and $\Delta S^{\neq} = (-43.2 \pm 3.2)\ \mathrm{J\,mol^{-1}\,K^{-1}}$ were determined. The exchange rate of the allyl ligands was estimated to be 1.0×10^4 Hz at ambient temperature on the basis of lineshape analysis. These data on **1** may be compared with data for Group 2 and Group 12 allyl compounds. The allyl exchange in bis(allyl)zinc in THF solution shows a $\Delta H^{\neq}$ value which is identical within limits of error.[20] However, a negative $\Delta S^{\neq}$ value of only $(-16 \pm 3)\ \mathrm{J\,mol^{-1}\,K^{-1}}$ has been reported for this reaction. The allyl exchange reaction in compound **1** runs through a transition state that is significantly more ordered compared to bis(allyl)zinc. Consequently, the allyl exchange rate of bis(allyl)zinc is much higher than that in compound **1**. The $\Delta G^{\neq}$ values for the allyl exchange in allyl magnesium halides in diethyl ether solutions is significantly smaller.[21] This leads to a higher allyl exchange rate in allyl magnesium halides than in compound **1**.

To compare a system containing an allylcalcium monocation with the neutral parent compound, $[\mathrm{Ca}(\eta^3\text{-}\mathrm{C_3H_5})_2]$, bis(allyl)calcium was reacted with bis(allyl)zinc in THF. The resulting product was isolated as an oil with the composition $[\mathrm{CaZn(C_3H_5)_4(thf)_2}]$ (**2**). Like compound **1**, the ^{1}H and ^{13}C NMR spectra of **2** show one set of signals for the allyl ligands at ambient temperature. VT ^{1}H NMR measurements in $[\mathrm{D_8}]$THF show the ionic structure of **2** in solution. The coalescence temperature of −60 °C is significantly lowered compared to compound **1**; that is, the crown ether ligand causes a decrease of the allyl exchange rate in the $[\mathrm{Ca(C_3H_5)}]^+[\mathrm{Zn(C_3H_5)_3}]^-$ system. The fundamental reactivity patterns of nucleophilicity and Lewis acidity of compound **2** differ from those of the neutral parent compound bis(allyl)calcium. Whereas **2** can be stabilized by [18]crown-6 (to form compound **1**), bis(allyl)calcium reacts with this ligand under release of propene at ambient temperature, thus showing its higher nucleophilicity. The triglyme adduct of **2**, a compound of the chemical formula $[\mathrm{CaZn(C_3H_5)_4(triglyme)}]$ (**3**), was isolated as an oil. Like **1** and **2**, this compound displays an ionic structure in THF solution, as shown by VT ^{1}H NMR spectroscopy. The resonances owing to the chelating ligand in the ^{1}H NMR spectrum of **3** are shifted significantly downfield compared to the neutral parent compound $[\mathrm{Ca}(\eta^3\text{-}\mathrm{C_3H_5})_2(\mathrm{triglyme})]$, indicating the higher Lewis acidity of **2**.[5b]

Attempts to grow crystals of **2** suitable for single-crystal X-ray analysis at low temperatures were unsuccessful. Crystallization of the 2-methylallyl derivative $[\mathrm{CaZn(CH_2C(CH_3)CH_2)_4(thf)}]$ (**4**) led to an ionic product of the formula $[\mathrm{Ca(thf)_6}][\{\mathrm{Zn}(\eta^1\text{-}\mathrm{CH_2C(CH_3)CH_2})_3\}_2]$ that had formed by a Schlenk equilibrium (see the Supporting Information). Thus, a chelating ligand such as the crown ether in **1** seems crucial to maintain the monoionic structure of the $[\mathrm{Ca(C_3H_5)}]^+[\mathrm{Zn(C_3H_5)_3}]^-$ system in the solid state.

In contrast to bis(allyl)calcium, **1** or other compounds formed in situ that contain an allyl calcium monocation do not polymerize 1,3-butadiene under conditions used for bis(allyl)calcium.[5b] This observation was ascribed to the decreased nucleophilicity of the allyl calcium monocation and hints at an anionic mechanism of the butadiene polymerisation initiated by $\mathrm{Ca}(\eta^3\text{-}\mathrm{C_3H_5})_2$.

In summary, we have synthesized and characterized a compound that contains a discrete allyl calcium monocation, $[\mathrm{Ca}(\mu^2\text{-}\eta^1\text{:}\eta^1\text{-}\mathrm{C_3H_5})([18]\mathrm{crown\text{-}6})]^+[\mathrm{Zn}(\eta^1\text{-}\mathrm{C_3H_5})_3]^-$ (**1**). This compound contains the first example of a ligand with a delocalized π-electron system that interacts with a calcium center exclusively by an η^1 binding mode. Furthermore, the cation in **1** shows an unusual non-bent coordination geometry. In agreement with earlier work,[13] this provides experimental evidence that the energy difference between linear and bent coordination geometries in organocalcium compounds is relatively small.

Experimental Section

1: A solution of bis(allyl)calcium (32 mg, 0.26 mmol) in THF (0.5 mL) was treated with a solution of bis(allyl)zinc (39 mg, 0.26 mmol) in THF (1 mL) at ambient temperature. A solution of [18]crown-6 (70 mg, 0.26 mmol) in THF (1 mL) was added. All volatiles were removed from the reaction mixture to give a pale yellow oil. After washing with diethyl ether/pentane (1:2; 2 × 3 mL), an off-white solid was obtained, which was dried in vacuo. Yield: 135 mg (0.25 mmol, 96 %).

^{1}H NMR (400.1 MHz, $[\mathrm{D_8}]$THF, 25 °C): $\delta = 2.50$ (d, $^3J_{\mathrm{HH}} = 11.3$ Hz, 16 H, $\mathrm{C}\mathit{H}_2\mathrm{CHC}\mathit{H}_2$), 3.86 (s, 24 H, $\mathrm{O(CH_2)_2O}$), 6.23 ppm (quint, $^3J_{\mathrm{HH}} = 11.3$ Hz, 4 H, $\mathrm{CH_2C}\mathit{H}\mathrm{CH_2}$). ^{1}H NMR (400.1 MHz, $[\mathrm{D_8}]$THF, −80 °C): $\delta = 2.16$ (d, $^3J_{\mathrm{HH}} = 8.7$ Hz, 2 H, $\mathrm{Ca((C}\mathit{H}^{\mathrm{a}}\mathrm{H^b)CH(C}\mathit{H}^{\mathrm{a}}\mathrm{H^b))}$), 2.43 (d, $^3J_{\mathrm{HH}} = 15.0$ Hz, 2 H, $\mathrm{Ca((CH^a}\mathit{H}^{\mathrm{b}}\mathrm{)CH(CH^a}\mathit{H}^{\mathrm{b}}\mathrm{))}$), 2.50 (d, $^3J_{\mathrm{HH}} = 11.2$ Hz, 12 H, $\mathrm{Zn(C}\mathit{H}_2\mathrm{CHC}\mathit{H}_2\mathrm{)_3}$), 3.75 (br m, 12 H, $\mathrm{O(C}\mathit{H}^{\mathrm{a}}\mathrm{H^b)O}$), 3.91 (br m, 12 H, $\mathrm{O(CH^a}\mathit{H}^{\mathrm{b}}\mathrm{)O}$), 6.16 (quint, $^3J_{\mathrm{HH}} = 11.2$ Hz, 3 H, $\mathrm{Zn(CH_2C}\mathit{H}\mathrm{CH_2)_3}$), 6.32 ppm (tt, $^3J_{\mathrm{HH}} = 8.7$ Hz, $^3J_{\mathrm{HH}} = 14.8$ Hz, 1 H, $\mathrm{Ca((CH^aH^b)C}\mathit{H}\mathrm{(CH^aH^b))}$). $\{^1\mathrm{H}\}^{13}$C NMR (100.6 MHz, $[\mathrm{D_8}]$THF, 25 °C): $\delta = 59.65$ (s, $\mathit{C}\mathrm{H_2CH}\mathit{C}\mathrm{H_2}$), 70.77 (s, $\mathrm{O(CH_2)_2O}$), 149.25 ppm (s, $\mathrm{CH_2}\mathit{C}\mathrm{HCH_2}$). $\{^1\mathrm{H}\}^{13}$C NMR (100.6 MHz, $[\mathrm{D_8}]$THF, −80 °C): $\delta = 57.92$ (br s, $\mathrm{Ca(}\mathit{C}\mathrm{H_2CH}\mathit{C}\mathrm{H_2))}$), 59.95 (br s, $\mathrm{Zn(}\mathit{C}\mathrm{H_2CH}\mathit{C}\mathrm{H_2))}$), 70.44 (br s, $\mathrm{O(CH_2)_2O}$), 148.01 (br s, $\mathrm{Ca(CH_2}\mathit{C}\mathrm{HCH_2))}$), 149.27 ppm (s, $\mathrm{Zn(CH_2}\mathit{C}\mathrm{HCH_2))}$). ^{13}C NMR (100.6 MHz, $[\mathrm{D_8}]$THF, −80 °C): $\delta = 57.92$ (ddd, $^1J_{\mathrm{CH}} = 142.6$ Hz, $^1J_{\mathrm{CH}} = 153.7$ Hz, $^2J_{\mathrm{CH}} = 13.9$ Hz, $\mathrm{Ca(}\mathit{C}\mathrm{H_2CH}\mathit{C}\mathrm{H_2))}$), 59.95 (br t, $^1J_{\mathrm{CH}} = 137.2$ Hz, $\mathrm{Zn(}\mathit{C}\mathrm{H_2CH}\mathit{C}\mathrm{H_2))}$), 70.43 (t, $^1J_{\mathrm{CH}} = 144.6$ Hz, $\mathrm{O(CH_2)_2O}$), 148.00 (br d, $^1J_{\mathrm{CH}} = 135.0$ Hz, $\mathrm{Ca(CH_2}\mathit{C}\mathrm{HCH_2))}$), 149.27 ppm (d quint, $^1J_{\mathrm{CH}} = 140.1$ Hz, $^2J_{\mathrm{CH}} = 2.9$ Hz, $\mathrm{Zn(CH_2}\mathit{C}\mathrm{HCH_2))}$). Anal. calcd (%) for $\mathrm{C_{24}H_{44}CaO_6Zn}$ ($534.09\ \mathrm{g\,mol^{-1}}$): (Ca + Zn) 19.75; found: (Ca + Zn) 19.69.

CCDC 805675 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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