Organocalcium Compounds

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Synthesis and Structural Characterization of Butadienylcalcium-based Heavy Grignard Reagents and a $Ca_4[O]$ Inverse Crown Ether Complex

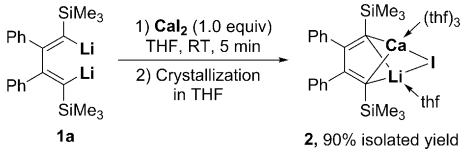
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Abstract: *The structure elucidation of heavy Grignard reagents (RAeX, Ae = Ca, Sr, and Ba, X = halides) has been greatly strived after, mainly because of their inaccessibility and remarkable instability. The synthesis of a series of butadienylcalcium compounds is presented, including 1-calcio-4-lithio-1,3-butadiene, 1,4-dicalcio-1,3-butadiene, and a $Ca_4[O]$ inverse crown ether complex, via the reaction between 1,4-dilithio-1,3-butadienes and calcium iodide in THF. Single-crystal X-ray analysis of these unprecedented heavy Grignard reagents revealed unique structural characteristics and bonding modes. Preliminary reaction chemistry was investigated. This study provides a novel class of alkenyl heavy Grignard reagents and a useful synthetic strategy for otherwise unavailable reactive organometallic compounds.*

Grignard reagents have been established as one of the most versatile reagents in organometallic and synthetic chemistry.[1] However, as the congener derivatives in Group 2, heavy Grignard reagents (RAeX, Ae = Ca, Sr, and Ba, X = halides) and the related chemistry are still in their infancy.[2] Current study centers on the synthetic utilities of heavy Grignard reagents generated in situ, in which the reactive species mostly remain elusive.[3] Thus, it still remains great demand and challenge for the structure elucidation of heavy Grignard reagents or corresponding reaction intermediates in this area. In contrast to the certain abundance of alkyl and alkynylcalcium compounds,[4,5] the efforts for the synthesis and characterization of (sp^2)C–Ca σ-bonded derivatives are rather unrequited, which is mainly due to their inaccessibility, high reactivity, and remarkable kinetic lability in solutions.[6] Some noteworthy contributions were made by Westerhausen and co-workers, who successfully characterized a series of arylcalcium halides from the reactions between activated calcium and aryl halides.[7] In 2014, Westerhausen and co-workers reported the first alkenylcalcium iodide based on the specific 1,2-dihydronaphthalene skeleton,[8] which is hitherto the only crystallographic characterization of a typical alkenyl-type heavy Grignard reagent.

We have been working on the chemistry of butadienyl organo-dimetallic reagents[9] and have proposed the formation of butadienyl heavy alkaline-earth-metal σ-bonded compounds as reactive intermediates.[3e–g] As our continued effort, we applied the cooperative stabilizing ability of butadienyl skeletons and successfully synthesized in this work a series of butadienylcalcium compounds, including 1-calcio-4-lithio-1,3-butadiene, 1,4-dicalcio-1,3-butadiene, and a $Ca_4[O]$ inverse crown ether complex, via the reaction between 1,4-dilithio-1,3-butadienes and CaI_2 in THF. In particular, the THF molecule was found to be degraded in an unconventional manner by virtue of the synergistic effect of dicalcium reagents,[10,11] resulting in the novel inverse crown ether complex with the expanded category of bonding anions and metal cations.[12]

As given in Scheme 1, the reaction of **1a** with 1.0 equiv of CaI_2 in THF at room temperature proceeded smoothly and was complete within 5 min, affording a clear dark red



1a

2, 90% isolated yield

Scheme 1. Synthesis of iodide-bridged 1-calcio-4-lithio-1,3-butadiene complex **2**.

solution, from which red crystalline compound **2** precipitated when kept at −28 °C with exposure to hexane vapor for a week. When 1.5 or 2.0 equiv of CaI_2 were used, compound **2** was also formed as the major product, which indicated that this heterobimetallic (Ca/Li) compound **2** was a preferred form. It should be noted that other calcium halides such as $CaBr_2$, $CaCl_2$, or common solvents such as diethyl ether, toluene, or n-hexane resulted in incomplete reactions, which is probably due to low solubility.

The ^{13}C NMR spectrum of **2** in [D_8]THF showed a singlet at $\delta = 204.4$ ppm assignable to the two carbon atoms bonded with the metal centers, and a singlet at $\delta = 168.2$ ppm assignable to the other two carbon atoms of the butadienyl skeleton. Single-crystal X-ray structural analysis of **2** revealed a monomeric structure (Figure 1) in which a typical alkenylcalcium iodide was involved. The Ca and Li centers lie on the opposite side of the C1-C2-C3-C4 plane, and are simultaneously bridged by an iodide and two carbon atoms (C1 and C4) of the butadienyl skeleton. The lengths of two (sp^2)C–Li

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Supporting information for this article (experimental details, X-ray crystallographic data, NMR spectra of all new products) can be found under https://doi.org/10.1002/anie.201704176.

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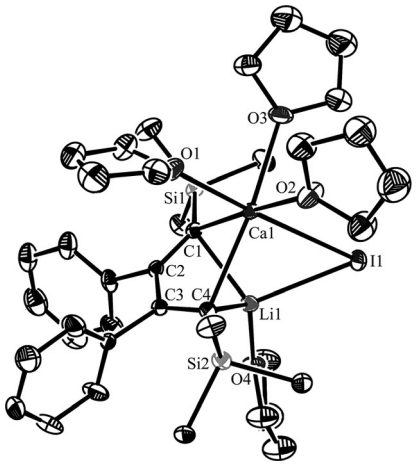
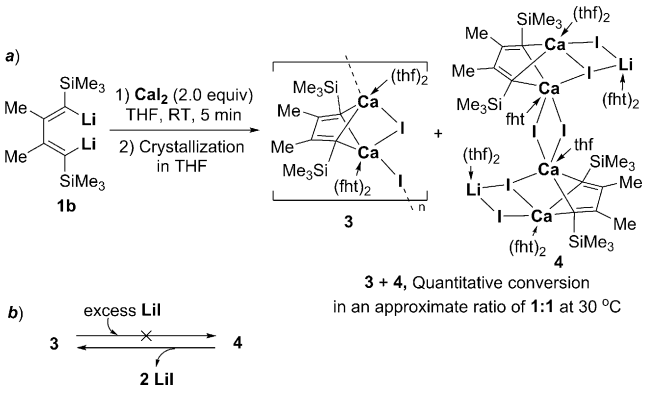


Figure 1. ORTEP drawing of **2** with ellipsoids set at 30% probability.[18] Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C2 1.349(7), C2–C3 1.534(7), C3–C4 1.355(7), C1–Li1 2.260(10), C4–Li1 2.145(10), C1–Ca1 2.569(5), C4–Ca1 2.568(5), Ca1–I1 3.2238(11), Li1–I1 2.838(9); C1-Ca1-C4 69.99(16), C1-Li1-C4 83.9(3).

bonds are 2.260(10) Å and 2.145(10) Å, which are comparable to those of **1a**.[3e] The lengths of two (sp^2)C–Ca bonds and Ca–I bond are 2.569(5) Å, 2.568(5) Å, and 3.2238(11) Å, respectively, which are a little longer than those in the reported 1,2-dihydronaphth-4-ylcalcium iodide (2.530(4) Å and 3.1863(8) Å, respectively).[8a] The C1-Ca-C4 bite angle (69.99(16)°) is somewhat smaller than those of the reported double bridges (for example, C-Mg-C angle 81.17(6)° in Mg/Li double bridge; C-Rh-C angle 82.9(3)° in Rh/Li double bridge),[13] which is mainly due to the somewhat longer C–Ca distances.

The substituents on the butadienyl skeleton were found to have a remarkable effect on the reaction process and the product structure. Thus, as shown in Scheme 2 a, when the 2,3-dimethyl substituted dilithio compound **1b** was treated with CaI_2 in THF, regardless of the amount (0.5–3.0 equiv) of CaI_2 used, a mixture of two products **3** and **4** were always generated. Products **3** and **4** were formed quantitatively as a 1:1 molar ratio mixture when the dilithio compound **1b** was treated with 2 equiv of CaI_2 in THF at 30 °C. From THF



Scheme 2. Synthesis of iodide-bridged 1,4-dicalcio-1,3-butadiene complexes **3** and **4**.

solution, red crystals of **3** precipitated together with orange crystals of **4**. However, from toluene/THF (20:1) mixed solvent, compound **4** crystallized as the major product, facilitating the isolation of pure **4**. In any case, suitable crystals of both **3** and **4** for X-ray single-crystal structural analysis could be facilely obtained.

Compound **3** was structurally characterized to be an iodide-bridged butadienyldicalcium complex, in which two alkenylcalcium iodides are involved (Figure 2). A one-dimensional linear structure is formed in the space via the head-to-tail linkage of the terminal iodide unit (Supporting Information, Figure S2). The lengths of (sp^2)C–Ca bonds are in the range from 2.545(6) Å (C4–Ca2) to 2.584(6) Å (C1–Ca2), which are close to those of **2**. The short distance between Ca1 and Ca2 (3.3632(18) Å) indicates a weak Ca–Ca interaction.[14] The bite angles 70.6(2)° (C1-Ca1-C4) and 70.2(2)° (C1-Ca2-C4) are also relatively small but close to that of **2**. The structure of **4** shown in Figure 3, the structural parameters of which are close to those of **3**, can be interpreted as a dimer of **3** with the ligation of 2.0 equiv of LiI. The iodide bridges in these organodicalcium compounds might play an important role in stabilizing the structures by restraining the well-known ligand redistribution process from these heteroleptic RCaI to homoleptic CaR_2 and CaI_2 (Schlenk equilibrium observed for magnesium).[15] The unprecedented RCaI·LiI moiety in **4** is analogous to the structure of the so-called turbo-Grignard reagents (RMgCl·LiCl; R = alkyl and amido) established by Knochel and co-workers,[16] which, to a certain degree, might inspire further research.

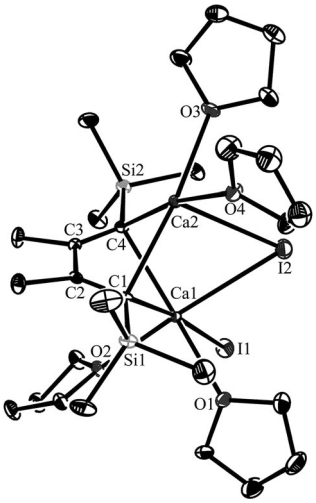


Figure 2. ORTEP drawing of the repeating unit of **3** with ellipsoids set at 30% probability.[18] Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C2 1.359(10), C2–C3 1.539(9), C3–C4 1.368(10), C1–Ca1 2.549(7), C4–Ca1 2.558(6), C1–Ca2 2.584(6), C4–Ca2 2.545(6), Ca1–I1 3.1891(13), Ca1–I2 3.1515(14), Ca2–I2 3.1723(14), Ca1–Ca2 3.3632(18); C1-Ca1-C4 70.6(2), C1-Ca2-C4 70.2(2).

It is noteworthy that when pure **4** in the crystalline form was dissolved in [D_8]THF at 30 °C, signals for both **3** and **4** in the ^{1}H NMR spectrum were observed, demonstrating that **4** partly disaggregated to generate **3** in THF solvent

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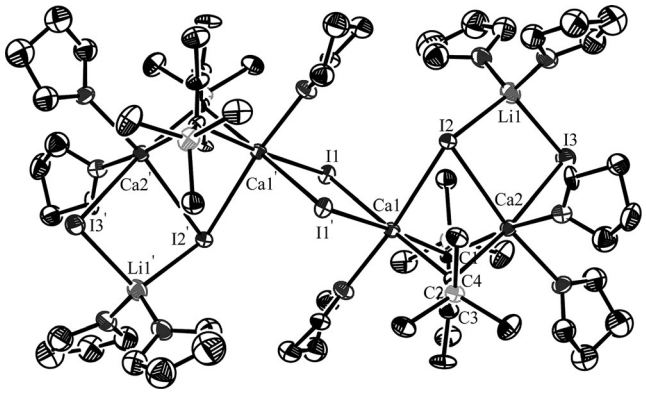
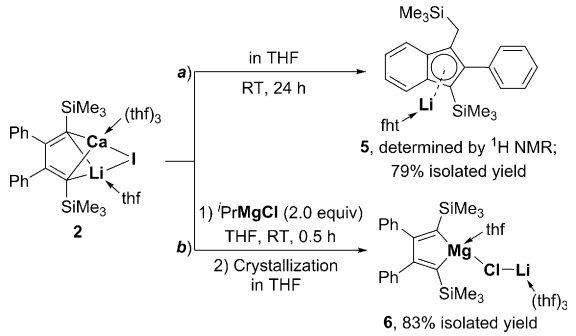


Figure 3. ORTEP drawing of **4** with ellipsoids set at 30% probability.[18] Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Ca1–I1 3.1955(19), Ca1–I1′ 3.1812(18), Ca1–I2 3.2084(18), Ca2–I2 3.2464(19), Ca2–I3 3.197(2), C1–Ca1 2.522(8), C4–Ca1 2.574(9), C1–Ca2 2.552(9), C4–Ca2 2.544(10).

(Scheme 2b). However, the inverse transformation from **3** to **4** was not observed even with excess LiI added. Variable-temperature ^{1}H NMR spectroscopy was carried out to investigate the transformation between compounds **3** and **4** (see the Supporting Information for details). With increasing temperature, the amount of product **3** increased while the amount of product **4** decreased, indicating that **4** should be first generated from the reaction between **1b** and CaI_2, followed by transforming to **3** along with the release of LiI salts.

With the above butadienyl heavy Grignard reagents in hand, we envisioned that their unique structures may lead to characteristic reactions. In compounds **2**–**4**, the large ionic radius of Ca^{2+} renders rather small bite angles to increase the skeleton strain, and the high electropositivity of Ca^{2+} makes the (sp^2)C–Ca bonds more ionic and reactive. Under certain reaction conditions, the bridges in compounds **2**–**4** might be broken to induce subsequent reactions.

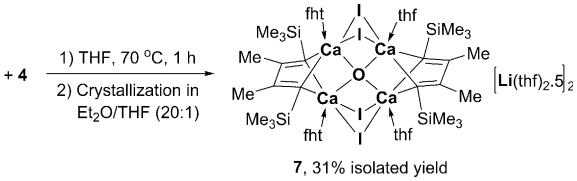
As indicated in Scheme 3a, when the THF solution of **2** was stirred at room temperature for 24 h, the indenyllithium complex **5** was generated as determined by ^{1}H NMR analysis. In our previous study on calcium iodide promoted direct transformation of **1a** into indene derivative, complex **5** was fully characterized as a dimeric indenyllithium structure.[3g] Thus, the reaction result shown in Scheme 3a demonstrated



Scheme 3. Synthesis of the indenyllithium **5** and LiCl-ligated magnesiacyclopentadiene **6**.

that this heterobimetallic (Ca/Li) compound **2** was the intermediate in the calcium iodide promoted direct transformation of **1a** to **5** (for a proposed transformation process, see the Supporting Information). Furthermore, the transmetalation reaction of **2** with 2.0 equiv of isopropylmagnesium chloride in THF at room temperature for 0.5 h provided exclusively the LiCl ligated magnesiacyclopentadiene **6** in 83% isolated yield (Scheme 3b). The complex **6** was characterized by NMR spectroscopy and single-crystal X-ray analysis (Supporting Information, Figure S4). A tandem double transmetalation/Schlenk equilibrium process might be involved in this reaction leading to the formation of **6**.

As described above, complex **4** was gradually disaggregated toward complex **3** with the rise of temperature. Thus we wondered if **4** could be completely transformed into **3** after a long time at an elevated temperature. Therefore, as shown in Scheme 4, the mixture of **3** and **4** generated in situ in THF



Scheme 4. Synthesis of the inverse crown ether complex **7**.

was stirred at 70 °C for 1 h and a deep red solution was afforded. Recrystallization in Et_2O/THF (20:1) solution yielded light red crystals of **7** suitable for X-ray structural analysis, which revealed a highly symmetrical structure (Supporting Information, Figure S5). The central framework of **7** indicates a novel Ca_4[O] inverse crown ether (Figure 4).

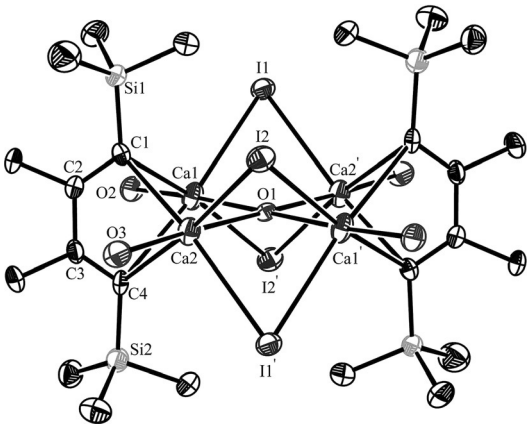


Figure 4. ORTEP drawing of the central anionic framework of **7** with ellipsoids set at 30% probability.[18] Hydrogen atoms, carbon atoms in coordinated THF molecules and peripheral counterions are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C2 1.329(14), C2–C3 1.542(15), C3–C4 1.304 (13), C1–Ca1 2.644(10), C4–Ca1 2.909(10), C1–Ca2 2.671(10), C4–Ca2 2.723(10), Ca1–I1 3.230(3), Ca1–I2′ 3.237-(2), Ca2–I2 3.172(3), Ca2–I1′ 3.247(2), Ca1–Ca2 3.093(3), Ca1–Ca2′ 3.515(3), Ca1–O1 2.332(2), Ca2–O1 2.349(2), Ca1–O2 2.366(8), Ca2–O3 2.361(8); C1-Ca1-C4 67.5(3), C1-Ca2-C4 70.0(3), Ca2-Ca1-Ca2′ 90.38(7), Ca1-Ca2-Ca1′ 89.62(7), Ca1-O1-Ca2 82.70(8), Ca1-O1-Ca2′ 97.30(8).

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The (sp^2)C–Ca bonds and Ca–I bonds in **7** are uniformly lengthened in comparison to those in **3**. The Ca centers are located nearly at four vertices of a rectangle in which the oxide (O^{2-}) lies in the centroid. The bonds Ca1–O1 (2.332(2) Å) and Ca2–O1 (2.349(2) Å) are a little shorter than bonds Ca1–O2 (2.366(8) Å) and Ca2–O3 (2.361(8) Å), which probably resulted from the electrostatic interaction between Ca^{2+} centers and O^{2-}. Two butadienyl dianions and four iodides are present as bridging moieties, while four calcium atoms serve as Lewis acidic centers. This structure is greatly highlighted by the expanded category of bonding anions and metal cations in an inverse crown ether.[11,12]

The O^{2-}-centered organometallic compounds have been well-documented in organolanthanide and organocalcium chemistry, in which the encapsulated O^{2-} are mostly believed to arise from the degradation of THF.[17] A tentative mechanism for the generation of **7** was proposed (for details see Supporting Information) mainly based on a seminal contribution by Mulvey and co-workers,[12b,c] who reported an inverse crown ether complex derived from bimetallic induced fragmentation of THF.

In summary, we have synthesized and structurally characterized a series of unprecedented butadienylcalcium compounds, which will make a good contribution to main-group organometallic chemistry. A novel inverse crown ether complex with expanded category of bonding anions and metal cations was revealed. Further applications of these butadienyl heavy Grignard reagents in organometallic and organic synthesis can be expected.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: butadienylcalcium compounds · heavy Grignard reagents · inverse crown ether · organocalcium compounds

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