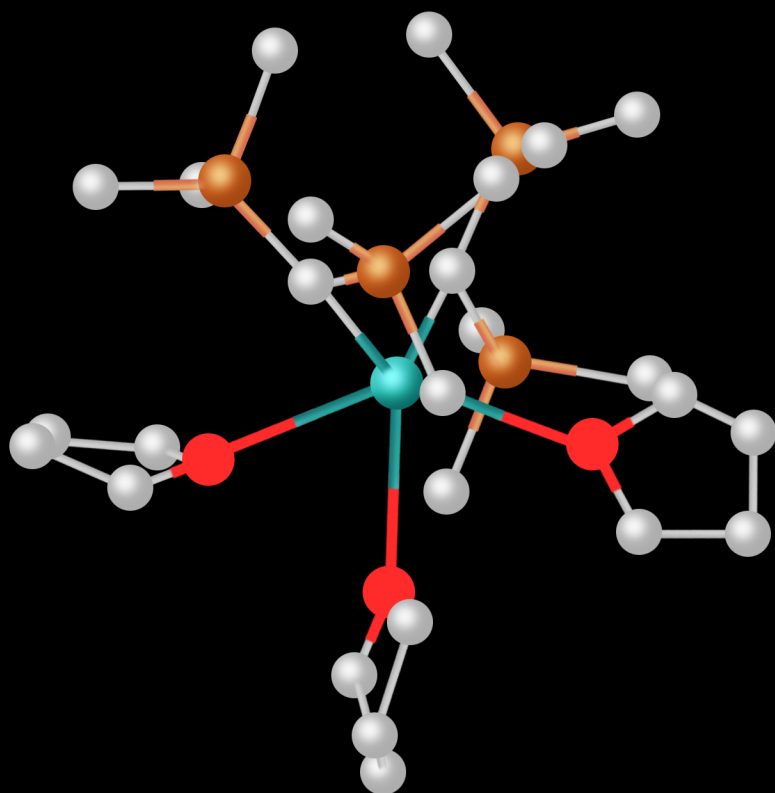


**THE SYNTHETIC
METHODS, STRUCTURES,
AND PROPERTIES OF THE
Ca-C σ BOND ORGANOCALCIUM
CONTAINING COMPOUNDS**



**Nejib Ben Hussein Mekni
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Bentham Books

The Synthetic Methods, Structures, and Properties of the Ca-C σ Bond Organocalcium Containing Compounds

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ISBN (Online): 978-981-5040-64-7

ISBN (Print): 978-981-5040-65-4

ISBN (Paperback): 978-981-5040-66-1

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First published in 2022.

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PREFACE

The organocalcium compounds may include organic compounds that contain calcium atom(s) in their molecular formula, in which calcium is not bonded to carbon atoms, but generally bonded to a heteroatom (*e.g.* O, N, S, *etc.*) as an ionic bond or coordinated to heteroatoms as complexes.

As a contribution to the organometallic field and especially the organocalcium chemistry, the organocalcium compounds that contain Ca-C σ -bond are described here. The main problems encountered in the synthesis of such compounds compared to their homologous organomagnesium derivatives are expected to be due to the low reactivity of calcium element, the low solubility in common solvents and the high reactivity of the formed intermediates and products and their instability, are detailed and discussed.

We scanned the different Ca-C σ -bond containing organocalcium compounds and compared some of their properties to those of the alkaline and alkaline earth organometallic homologous compounds.

In this work, several important notes such as the restriction of the Ca-C double bond from real experimental examples are highlighted. Calcium may form two σ -bonds with two different carbon atoms in very difficult geometrical situations in the presence of high hindrances under the effect of bulky groups, but it cannot form a double bond. Besides, many interesting ideas such as degrading agent property, organocalcium spectroscopy and others are discussed.

In addition to research groups in the academic field of organometallic compounds, many other readers may benefit from this book reference as well as the catalyst, polymer, petroleum, pharmacology and pipeline fields, especially in the scarcity of reference books on the subject.

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CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The author declares no conflict of interest, financial or otherwise.

ACKNOWLEDGEMENTS

Declared none.

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ACKNOWLEDGEMENTS

The authors would like to thank their colleague Dr. Amr Eddeck, a member of Taibah University teaching and research staff (Saudi Arabia), Miss Nour El Houda Mekni and the professor Sliman Ben Ghorbal for their helpful technical efforts and Pr. Dr. Mohamed Abderrahmane Sanhoury, Ph.D., MRSC (Member of the Chemical Royal Society) for technical and language assistance.

We thank all our professors from the Faculty of Sciences of Tunis (Tunisia), all our colleagues, and all our teachers.

We dedicate this work to the Soul of our fathers, our mothers, our wives and all our family members.

General Introduction

Abstract: This first chapter is a general introduction to the book in which we give a background on the Ca-C σ -bond containing organocalcium compounds, which are less studied as compared to other organometallic compounds.

We describe the interest in synthesizing the synthesized organometallic intermediates and products as well as their application fields such as chemistry, biology, medicine, pharmacology, and industry.

It is indicated that such compounds are not well-known because of the low reactivity of calcium elements, the low solubility of organocalcium intermediates and products in common organic solvents, their instability resulting from their high reactivity, cause their degradation and the degradation of their preferred ethereal solvents.

Despite the significant difference in electronegativity value between the two elements, the Ca-C σ -bonds have a covalent polar character. In many cases, the coordination considerably decreases the calcium electropositive character, facilitating the formation of the Ca-C σ -covalent bond.

The difficulties in synthesizing such compounds, their degradation property and catalytic behaviour as well as the spectroscopy technics used to identify their structures are also described.

Keywords: Alkylcalcium, Alkaline earth metals, Ca-C σ bond, Calcium, Calcium coordination, Catalytic properties, Calcium reactivity, Covalent bond, *d*- orbitals, Degradation, Ethereal solvents, Electronegativity, Intermediates, Ionic bond, Organometallic, Organocalcium, Phenylcalcium, Solvent degradation, Spectroscopic technics.

GENERAL INTRODUCTION

Organometallic compounds are increasingly attracting great interest as witnessed by the number of their newly synthesized intermediates and products, involving different applications, in chemistry, biology, medicine, pharmacology, and industry fields.

Compared to the other alkali, alkaline earth and transition element organometallic derivatives, the Ca-C σ -bond containing organocalcium compounds are less known for many reasons, which are related to the low reactivity of calcium element, the low solubility of the organocalcium intermediates and products in common organic solvents, their instability coming from their high reactivity, that causes their degradation and the degradation of their preferred ethereal solvents.

The high difference in electronegativity value between calcium and carbon elements could be expected to result in the formation of a Ca-C ionic bond. However, the observed Ca-C σ -bond confirms its polar covalent character. The formation of such bonds may be due to the high coordination number of calcium atom from its *d*-vacuum orbitals to both *n* lone electron pairs of heteroatoms of the main product as well as the ethereal solvents and to the π -bonding pairs. Such coordination would considerably decrease the calcium electropositive character, yielding the formation of a Ca-C σ -covalent bond.

From the above-described behavior, we were inspired in this work by the idea of grouping all information and the behavior of such compounds. So, our main goal is focused on the organocalcium compounds that contain Ca-C σ -bond.

Herein, we enumerate the synthetic methods and encountered difficulties, the structures, degradation and catalytic behaviour of such compounds and the spectroscopic techniques used to identify their structures.

We have grouped almost all kinds of previously synthesized Ca-C σ -bond containing organocalcium intermediates and products including alkylcalcium, allylcalcium, alkynylcalcium, diene calcium, diyne calcium phenylcalcium, benzylcalcium, arene calcium and heteronuclear aromatic calcium derivatives.

CONCLUSION

The polar covalent Ca-C σ -bond-containing compounds are less known than the other organometallic compounds; because of the different encountered problems, before, and during the synthetic process.

The *n* and π electron pairs of organic compounds coordinate to the *d*-vacuum orbitals of calcium atom, to decrease its electrophilicity and facilitate the formation of the Ca-C bond.

This work grouped all kinds of synthesized Ca-C σ -bond containing compounds, the encountered synthetic problems, and their solutions.

CHAPTER 2

Calcium Element

Abstract: In this second chapter, we have grouped the physical and chemical properties of elemental calcium and calcium cation species as well as their importance in the human body, especially in the skeleton and cell, as well as their applications in the chemical, electrical, and biological life fields.

In a nutshell, we describe the history of the organocalcium Ca-C σ -bond containing compounds.

Then, we expose the encountered challenges and difficulties in the synthesis of organocalcium Ca-C containing compounds: before, during and after the organocalcium preparation and the solutions to overcome these difficulties.

We have grouped the calcium activation methods, the nature of the solvent, the substrate structure, temperature and the optimal experimental reaction conditions.

Keywords: Alkali earth metal, Calcium element, Calcium-Carbon covalent bond, Calcium electron configuration, Calcium activation, Calcium electronegativity, Calcium isotopes, Calcium ion, Calcium *d*-orbitals, Calcium physical properties, Calcium chemical properties, Calcium-Carbon σ -bonding, Calcium reactivity, Covalent bonds, Organocalcium halides, *s*-bloc elements, Organocalcium Ca-C compounds, Organocalcium challenges, Organocalcium problems, Organometallics.

1. CALCIUM ELEMENT

1.1. Introduction

Calcium is the fifth most abundant element by mass in both Earth's crust and seawater (3.4%) [1 - 3] and the most abundant mineral in the human body. Likewise, calcium cation (Ca²⁺) is the fifth-most-inexhaustible dissolved seawater metallic ion by both mass and molarity [4, 5]. Calcium element was isolated for the first time by Humphry Davy in 1808 [6, 7]. It is the second alkaline earth metal in the periodic table, with two allotropes [8].

External to earth, two ionized calcium lines were detected (H- and K- lines at 3968.5 Å and 3933.7 Å, respectively) in the visible spectra of many stars, including the sun [9].

Calcium weighs more than 1 Kg in the adult human body. It is essential for living organisms, especially as a cellular ionic messenger, with many other functions, such as the stabilization of the endoskeleton. Particularly, the passage of the calcium through the cytoplasm represents the signal for many cellular processes, including cellular mobility, neuronal transmission as in excitatory synapse [10], fertilization [11], cell growth [12] or proliferation [12, 13], muscle contraction [14], learning [14, 15], memory [16, 17], and saliva secretion [18, 19]. The study of calcium flagging can be monitored by loading the cell's cytoplasm with a calcium-sensitive fluorescent dye for example Fura-2 [20, 21].

In its solid state (elemental metallic form), calcium is hazardous, causing violent reactions with water and acid contact (producing hydrogen [22]). Because of its high reactivity with oxygen and sulfur-containing impurities, calcium is also used in metallurgy as decarbonizer, deoxidizer, and desulfurizer to produce some alloys [23]. When lit, calcium burns in the air producing a high-intensity orange-red brilliant light.

Calcium ion and most calcium compounds, found in many foods and useful materials have low toxicity. But, a high calcium intake or absorption contributes to the development of kidney stones [24 - 26] and causes few serious health problems. When swallowed, calcium metal can be fatal [27]. In addition, some studies have suggested that excessive intake of calcium as supplements could cause an increased cardiovascular mortality [28 - 31]; however, other investigations found that there is no risk [32].

1.2. Calcium Physical Properties

Calcium is a silvery metallic element, extracted through electrolysis from calcium-containing compounds such as calcium chloride. It is harder than lead, with a lower electrical conductivity than aluminium and copper. It has potential uses as wiring in off-world applications [33] but its use in other application fields is limited by its high reactivity with air.

Among the known 26 isotopes of calcium (^{35}Ca to ^{60}Ca), there are five stable isotopes (^{40}Ca , ^{42}Ca , ^{43}Ca , ^{44}Ca , ^{46}Ca), one that has a long half-life (^{47}Ca) and a cosmogenic isotope (^{48}Ca), and one radioactive ^{41}Ca (Table 1).

Table 1. Some properties of calcium isotopes.

Isotope	Natural Abundance	Half-life	DM ^a	DE ^b (MeV)	DP ^c	s ^d
⁴⁰ Ca	96.941%	Stable				0
⁴¹ Ca	Trace	1.03 x 10 ⁵ y				7/2
⁴² Ca	0.647%	Stable				0
⁴³ Ca	0.135%	Stable				7/2
⁴⁴ Ca	2.086%	Stable				0
⁴⁵ Ca	Synthetic	162.7 d	β ⁻	0.258	⁴⁵ Sc	7/2
⁴⁶ Ca	0.004%	Stable				0
⁴⁷ Ca	Synthetic	4.536 d	β ⁻	0.694 1.99	⁴⁷ Sc	7/2
			γ	1.297		
⁴⁸ Ca	0.187%	4.3 x 10 ¹⁹ y	ββ ⁻	4.274	⁴⁸ Ti	0

^aDM: Decay Mode; ^bDE: Decay Energy; ^cDP: Decay Product; ^ds: Nuclear spin.

The electropositive character of calcium, (electronegativity value EN = 1.04 according to Pauling scale) makes it too reactive and consequently not found in nature in its elemental state. Exposed to the air, it quickly forms a white coating of calcium nitride and calcium oxide. So, in nature, it is found to be combined with other elements. Most calcium salts are colourless and the most abundant calcium compounds in the nature are CaCO₃, Ca(OH)₂, Ca₃(AsO₄)₂, CaCl₂, Ca(OC_l)₂, Ca(MnO₄)₂, Ca₃(PO₄)₂, Ca₃P₂, CaSO₄.2H₂O, CaWO₄, Ca₁₀(PO₄)₆(OH)₂, in which, calcium is considered as redox-inert with an oxidation state 2+. Some of the selected physical properties of the *s*-block metals (Lithium, Magnesium, Calcium and Strontium) are gathered in Table 2.

Table 2. Comparison of some selected physical properties of the *s*-block metals: Lithium, Magnesium, Calcium and Strontium [34].

	Lithium	Magnesium	Calcium	Strontium
Electronegativity ^a	0.97	1.23	1.04	0.89
1 st Ionization potential (eV)	5.320	7.642	6.111	5.695
2 nd Ionization potential (eV)	75.63	15.03	11.87	11.03
Electron affinity (eV)	-0.618	+0.4	+0.3	+0.3
Atomization enthalpy (KJ.mol ⁻¹)	159.37	147.70	178.2	164.4
M-M Bond energy (KJ.mol ⁻¹)	106	129	105	84
Hydration enthalpy (KJ.mol ⁻¹)	-521	-1992	-1577	-1415
Radius of metal ion (pm) ^{b,c}	90	86	114	132

(Table 2) cont....

	Lithium	Magnesium	Calcium	Strontium
Standard potential vs NHE E ₀ (V) ^b	-3.040	-2.356	-2.84	-2.89
Melting point (°C)	180.54	648.8	839	768
Boiling point (°C)	1347	1105	1482	1380

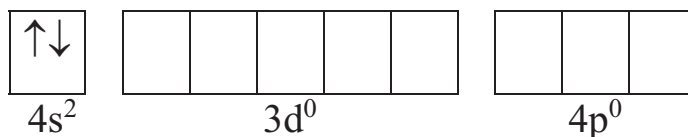
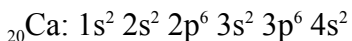
^a Allred-Rochow electronegativity values. ^b The values refer to monovalent lithium and divalent alkaline earth metals. ^c Radius of the hexacoordinate ion.

1.3. Calcium Chemical Properties

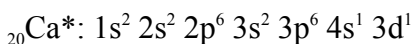
As previously mentioned, calcium atomic element is very reactive toward its stable ionic cation Ca²⁺. The ionic species Ca²⁺ comes from the easy loss of the two valence electrons and empty 4*s*-subshell orbital. As a result, calcium chemistry is nearly related to Ca²⁺ salts. The Ca²⁺ cation is “hard”, and thus has more affinity for oxide ligands. In life fields; this calcium cation constitutes the main problem in hard water: it forms insoluble deposits of carbonate in plumbing conducts. A cationic exchange with soap cation (generally Na⁺ or K⁺) produces a soap scum. When heated above 825 °C, calcium carbonate compound is converted into calcium oxide (CaO), which reacts vigorously with water to produce calcium hydroxide.

On the other hand, the existence of the 3*d*-subshell on the calcium atom, suggests the important participation of the *d*-orbitals in the structure of the molecular and complex calcium species. Ca²⁺ is relatively a large cation (~114 pm radius), that tends to have a high number of coordination ligands. For example in the calcium fluoride CaF₂ salt, each Ca²⁺ cation is surrounded by eight F⁻ ligands, and the structure of the polymeric [Ca(H₂O)₆]²⁺ center in hydrated calcium chloride, illustrates the high coordination number of calcium complexes.

The electron configuration and the quantum orbital diagrams of calcium atom represented in Scheme 1, illustrate the existence of eight vacant orbitals (5*d*- and 3*p*-orbitals), allowing eight coordination ligands.



In its activated form, calcium element ${}_{20}\text{Ca}^*$ have a 4*s*¹ 3*d*¹ electron configuration:



CHAPTER 3

Organocalcium (Ca-C) σ -bond Containing Compounds

Abstract: Compared to other organometallics, the number of organocalcium compounds and their related publications are limited. In this chapter, we grouped different Ca-C σ -bond containing organocalcium compounds described in the literature, (Alkyl, silyl, cycloalkyl, benzyl, alkenyl, alkynyl, diene, diyne, phenyl, biphenyl, anthracene, halo thiophene and picoline derivatives) with the specificity for each kind of compounds. We discuss the stabilizing factors of structures including: conjugation, hyperconjugation, complexing heteroatom lone pairs and π -bonding electron pairs.

The different synthetic processes used to avoid synthetic problems of substrate and calcium source reactivity, intermediate and product stability and solubility, reaction temperature, yields and decomposition reactions of both intermediates and products, as well as the orientation of the reaction sides in some reactions, are also grouped (thiophene and picoline derivatives).

The halo aromatic organocalcium compounds are described to be the most stable intermediates, giving the best yields.

Some calculations that correlate with experimental results are mentioned. Particular calcium reagents, such as Ca*, Ca₂ and particular reactions as well as exchange (transmetalation) reactions are also examined.

Some examples of the geometrical structures, which give C-Ca-C bent angles, and bond lengths obtained from X-ray are gathered.

Keywords: Activated calcium, Calcium complexes, Calcium coordination, Calcium derivatives, Calcium halides, Calcium halo intermediates, Calcium insertion reaction, Calcium-Carbon bent angle, Calcium-Carbon σ -bond, Direct and indirect synthesis, Ethereal coordination, Ethereal medium, Exchange reaction, Ipso-carbon atom, Metathesis reaction, Organocalcium complex, Organocalcium degradation, Organylcalcium, Schlenk equilibrium, Transmetalation.

1. Ca-C σ -BOND ALKYL CALCIUM COMPOUNDS

1.1. Introduction

Among the organic compounds, alkane derivatives are the less reactive organic groups. So, the alkyl organocalcium compounds are the most difficult to prepare, for many reasons.

The alkylcalcium compounds are generally stabilized from either silyl or aryl groups in α -positions, reducing the nucleophilicity due to reduced charge under hyperconjugation or charge delocalization effects.

According to Hartre-Fock theory, Kaupp *et al.* published in 1992 [1] their calculations on the simplest organocalcium, dimethylcalcium hydrocarbon. They showed that this compound has a linear geometry for C-Ca-C angle and a Ca-C bond length of 248.8 pm and a calcium atom charge of 1.78. Wolf *et al.* [2] synthesized this compound in 2018 from a metathesis reaction of methyllithium and calcium bis(trimethylsilyl)amide in diethyl ether (Scheme 6):

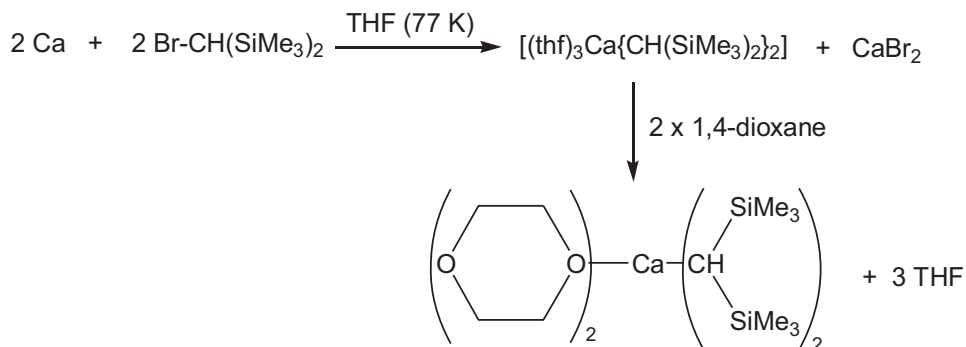


Scheme 6. Synthesis of calcium dimethyl compound.

The isolation, crystallization and structural characterization of CaMe_2 and MeCaX have not yet been reported. However, the monomethylcalcium prepared from dimethylmercury vapor transmetallation was characterized using gas phase procedures [3] or from laser technique in the presence of a vapor organic substrate [4].

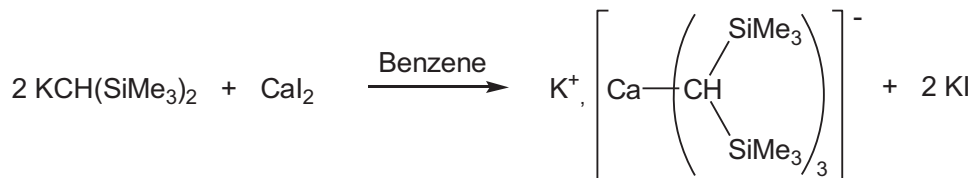
1.2. Silyl Substituted Methylcalcium Derivatives

The $(\text{Me}_3\text{Si})_2\text{CH-CaBr}$ product resulting from the calcium insertion reaction, was obtained *via* Schlenk equilibrium [5]. The co-condensation reaction of the bromobis(trimethylsilyl) methane with elemental calcium in THF at (77 K), yields the $(\text{thf})_3\text{Ca}(\text{CH}(\text{SiMe}_3)_2)_2$ compound, replacing the CaBr bond from coordination to three THF molecules and excluding a CaBr_2 species [5]. The addition of 1,4-dioxane to the product yields the replacement of the three coordinated THF molecules from two dioxane molecules (Scheme 7). Bonded to four groups (two dioxane and two methyl(disilyl(trimethyl)) groups), the calcium center is found in a distorted tetrahedral environment, linked to C and O atoms, with CaC (248.3 pm) and CaO (237.3 pm) bond lengths [5]. The high shielded ^1H NMR signal of the CH proton at $\delta = -1.74$ ppm justified the anionic methyne proton character [5].



Scheme 7. Reaction of bromo-bis(trimethylsilyl) methane with calcium in THF at 77 K and dioxane/THF coordination exchange.

In an irrespective reaction, the ionic calcium salt CaI_2 reacts with a potassium bis(trimethylsilyl) methanide suspension in benzene to yield the corresponding potassium-calcium ionic compound $\text{K}(\text{Ca}(\text{CH}(\text{SiMe}_3)_2)_3)$ (Scheme 8) [2]. The calcium species, part of the calciate anion $\text{Ca}(\text{CH}(\text{SiMe}_3)_2)_3^-$, shows an unexpected trigonal pyramidal environment, similar to the ytterbate anion structure [6], with C-Ca-C bond angles between 107.9° and 116.1° and Ca-C bond lengths of 247.4 pm to 255.6 pm. Later, this research group prepared the same ethereal complex ionic compound $(\text{thf})_3\text{KCa}[\text{CH}(\text{SiMe}_3)_2]_3$ from the metathesis reaction of $\text{Ca}(\text{OSO}_2\text{-C}_6\text{H}_4\text{-Me})_2$ with $\text{KCH}(\text{SiMe}_3)_2$ [7].



Scheme 8. Ionic potassium calciate $\text{Ca}(\text{CH}(\text{SiMe}_3)_2)_3^-$ obtained from the reaction of ionic calcium salt CaI_2 with a potassium bis(trimethylsilyl) methanide suspension in benzene.

When reacting the extremely bulky reagent, potassium tris(trimethylsilyl) methanide homologue of the potassium bis(trimethylsilyl)methanide, in the same experimental conditions, the metathesis reaction affords the corresponding solvent-free colorless compound $\text{Ca}(\text{C}(\text{SiMe}_3)_3)_2$ (Table 3), having a larger bent angle C-Ca-C 149.7° and a shorter Ca-C bond length of 245.9 pm (Scheme 9) [8]. The advanced calculations show a quasi-linear geometry molecular structure of the product. But in the solid state, the agonistic interactions between methyl groups and calcium species could explain the C-Ca-C bent geometry.

Coordination, Degrading Agent, Catalyst Property and Spectroscopy of Organocalcium Compounds

Abstract: In addition to the coordination of the calcium to the n electron pairs, some examples of coordination to the π electron pairs are observed resulting from calcium interactions with highly conjugated systems. The complex structures vary from ordinary to close to the unexpected organocalcium inverse sandwich.

The organocalcium Ca-C bond containing compounds are highly reactive. They degrade and act as degrading agents on the solvent. The study of the effect of five factors: temperature, concentration, organic group, counter ion and coordinated donor solvent, shows an intramolecular degradation mechanism. Organocalcium complexes are more stable in the THP than in the THF ethereal media.

Calcium and organocalcium Ca-C σ -bond containing derivatives are described as efficient pre-catalysts for catalytic conversions of alkenes by polymerization, hydroamination, hydrosilylation, hydrogenation, and hydrophosphination. The activation process is suggested as an electrostatic interaction between the alkene and Lewis acidic calcium metallic species, leading to both vertical and horizontal polarization of the π bond electron density, resulting in an incentive for nucleophilic attack. Some researchers illustrate that the organocalcium derivatives may be described as “Trojan horses”

X-ray constitutes the most efficient technique to characterize the organocalcium structures for crystalized compounds, affording interesting information about angle values and bond lengths.

The ^{43}Ca , ^{13}C and ^1H NMR spectroscopy constitutes an alternative, secondary and complementary tool for characterizing both soluble, and even insoluble compounds, monitoring the reaction progress and making specific experimental manipulations.

The coupling constants $^1J_{\text{Ca-C}}$, and $^2J_{\text{Ca-C-H}}$ are not mentioned and there is no mass spectrometry nor IR spectroscopy studies.

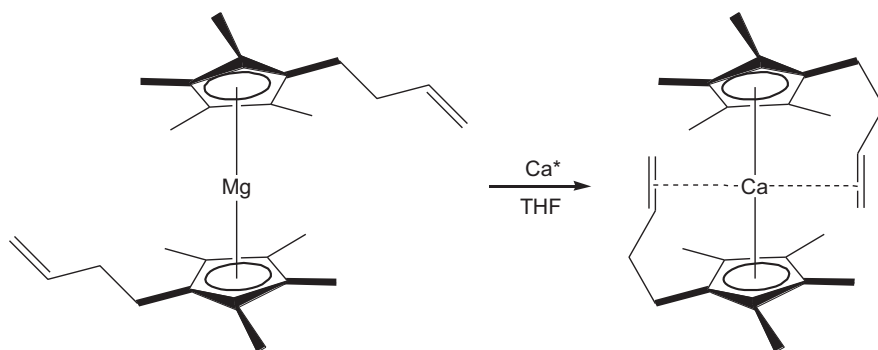
Keywords: Calcium ether cleavage THF, Degradation mechanism, Durability in ethereal solutions, Ether degradation, Hydroamination, Hydrosilylation, Ipso-Carbon atom, Lewis acid, Mixture titration, NMR reaction monitoring, NMR spectroscopy, Organocalcium catalyst, Organocalcium inverse sandwich complex,

π -Bond calcium coordination, π -Bond polarization, Polymerization reaction, THF degradation, THF α -deprotonation, Trojan horses, X-ray.

1. CARBON-CARBON π -BOND CALCIUM COORDINATION

The calcium-carbon bonding is limited to the Ca-C σ single bond. The formation of the Ca=C calcium-carbon double bond is forbidden because the 3*d* calcium orbitals overlapping with the *sp*² hybridized carbon atom orbitals is not possible due to great differences in both geometries and energy levels of the two orbitals. But, calcium atom favours the coordination to the π electron of carbon-carbon double bond pairs, involving empty *d* orbitals. Herein, we limit our description to some coordination examples of calcium atom to the π electron bonds, observed as a result of activated calcium atomic element interactions with highly conjugated systems and especially for aromatics.

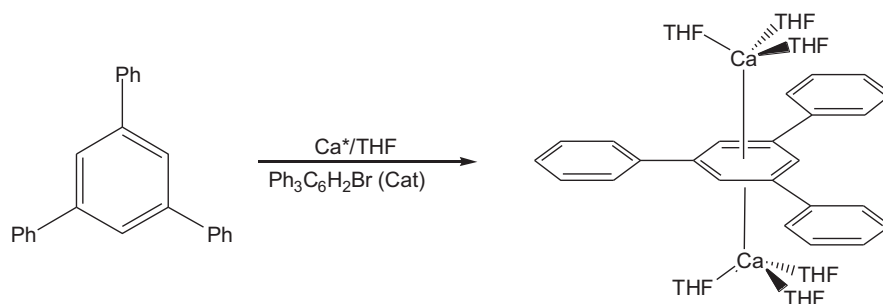
Because of the limited number of the magnesium atom coordinations, in the following structure, it coordinates only with the conjugated π electron pair cyclic bonds of the two *penta* substituted cyclopentadienes in a sandwich structure and do not interact with the two ethylenic π electron pair bonds (Scheme 38). When exchanged with the heavy metallic activated calcium atom in THF, the latter atom, in addition to the coordination to the π cyclic electron bonding pairs, it coordinates to the non-conjugated olefins tethered to cyclopentadienyl ligands through their π bonds (Scheme 38), yielding a close structure (cage) protecting the calcium atom from the contribution of its *d* orbitals, which do not exist for magnesium [1].



Scheme 38. Calcium atom coordination to the π cyclic electron bonding pairs, and to the non-conjugated olefin π bonds [2 - 6].

In the reaction of 2,4,6-Ph₃C₆H₂Br(tpb) with Ca* in THF, the common THF degradation products, ethene and vinylalcoholate, resulting from calcium insertion into the C-Br bond are identified from NMR analysis data [7 - 11].

In another arene reaction, the unexpected (thf)₃Ca{ μ -Ph₃C₆H₃}Ca(thf)₃ organocalcium inverse sandwich complex [12, 13] with two calcium atoms in either side of the arene ligand is obtained from the reaction of 1-bromo-2,4,6-triphenylbenzene with an excess of activated calcium metal in THF at -60 °C [8]. Realized in *d*₈-THF, the same reaction yields mono-deuterated triphenylbenzene anions, confirming that the first reaction step consists of an insertion reaction of Ca atom into the catalyst C-Br bond, followed by an ether cleavage and reduction reactions of THF by the excess of activated calcium metal, as well as the common degradation reactions for heavy Grignard reagents [7 - 11]. On the other hand, mixed together in THF activated calcium and 1,3,5-triphenylbenzene (1,3,5-Ph₃C₆H₃) react only after the addition of a catalytic amount of 2,4,6-Ph₃C₆H₂-Br acting as initiator and the product is obtained in a good yield (Scheme 39) [12].



Scheme 39. The unexpected (thf)₃Ca{ μ -Ph₃C₆H₃}Ca(thf)₃ organocalcium inverse Sandwich complex.

The obtained “inverse” sandwich complex with two Ca(I) atoms shows an unexpected unreactivity toward ether and exhibits no tendency to cleave ether, resembling the magnesium(I) compounds behavior that coordinate to THF molecules to form THF adducts without destroying the Mg-Mg bond [14]. This organocalcium complex exhibits strong reducing properties, but rather weak Lewis basicity due to charge delocalization (and hence nucleophilicity) of tpb²⁻

Conclusion

Abstract: Ca-C σ -bonds containing organocalcium compounds are prepared from different synthetic methods. Several difficulties and challenges are encountered before, during and at the end of the reaction.

Organocalcium derivatives are insoluble in common organic solvents and show degrading properties. Ethers are the solvents of choice and THF gave the best results.

The products are generally ethereal six-coordinated calcium centers (L₄CaRX), with a Ca-C bond length of around 250 pm, depending on many factors.

Arylcalcium derivatives are the easiest to prepare and are more stable than the other organocalcium compounds because of the conjugation effect phenomena. Ethereal solvents have a slight influence on the Schlenk-equilibrium type between RCaX or CaR₂ and CaX₂.

Almost all types of the main classes of σ -bond containing organocalcium derivatives are synthesized. Calcium carbon double bond was never formed.

X-ray analysis is the best technique for the characterization of crystallizable organocalcium compounds. The ⁴³Ca NMR does not provide interesting information about the structures. The ¹³C and ¹H NMR data constitute an interesting tool that contributes the elucidation of the structure of the organocalcium compounds, especially for the *non*-crystallized compounds.

Reactivity, chemical behaviour and ¹³C NMR chemical shift values of organocalcium complexes exhibit more similarities to the organolithium rather than the organomagnesium derivatives and were explained on the basis of their comparable electronegativity values.

Keywords: ⁴³Ca NMR, Acidity of α -hydrogen atoms, Activated calcium, Aliphatic carbanion nucleophilicity, Alkyl halides, Calcium carbon double bond, Calcium ligand coordination, Catalytic properties, Complex cation exchange., Insertion reaction, *ipso*-carbon atom, Lewis acidity of calcium species, Monomeric coordination species, Schlenk-equilibrium, Six-coordinate calcium centers, Synthetic challenges, The Ca-C bond length, THF, Wurtz coupling, X-ray.

Ca-C σ -bond containing organocalcium compounds are synthesized using different pathways, including insertion reaction of activated calcium with substrates, ionic calcium salt reactions complex cation exchange.

The development of the organocalcium derivatives represents an alternative to classical lithium and magnesium organic compounds. The availability of many organocalcium intermediates gives the possibility to explore the field of applications in stoichiometric reactions and catalysis.

The synthesis of such compounds encounters several difficulties and challenges before, during, and at the end of the reaction, which are related to several factors including substrates, intermediates and product reactivity, structure stability and solubility with some deviations.

Organocalcium derivatives are insoluble in common organic solvents. Ethers are the solvents of choice for the synthesis and reactions of organocalcium compounds because they stabilize them from the coordination of oxygen atom lone pairs to calcium species, and THF shows the best results. Although Ca-C σ -bond containing organocalcium compounds remain highly reactive, they act as degrading reagents in ethereal solvents. Such reactivity depends on temperature, ether (rings chain of the cyclic ether, acidity of α -hydrogen atoms, Lewis acidity of calcium species, nucleophilicity and basicity of the carbon atom bonded to calcium).

The obtained products are generally monomeric species, coordinated to ethereal solvent molecule, in a preferred six-coordinated calcium center (L₄CaRX). The Ca-C bond lengths are approximately 250 to 260 pm, depending on many factors, especially on the calcium ligand coordination number, the basicity of the ligands and their bulkiness.

Arylcalcium derivatives are the easiest to prepare among organocalcium compounds and are more stable than the other derivatives because of the effect of conjugation phenomena. Alkyl halides may be considered to belong more to Wurtz coupling reactions type rather than aryl halides which extend to the trimethylsilane methyl iodides and bromides. In addition, the substituent nature and positions on the aryl group may affect the reaction time and yield, thus methyl substituent can be deprotonated and yield the benzylic product. The bulky alkyl groups such as *t*-Bu- in *ortho*- position may hinder the reaction and *para*- phenyl substituents may render the isolation of the product difficult.

On the other hand, trimethylsilyl and phenyl groups decrease considerably the nucleophilicity of the aliphatic carbanion, yielding trimethylsilylmethyl- and

benzylcalcium complexes. Etheral solvents influence slightly the Schlenk-equilibrium type between RCaX or CaR₂ and CaX₂.

Almost all types of the main class of σ -bond containing organocalcium derivatives are synthesized. Both intermediates and products show interesting catalytic properties, especially in the polymerization reaction of alkenes.

Calcium carbon double bond was never formed. That calcium species may support high steric repulsions from bonding to two different carbon atoms in the presence of their bulky repulsive neighbors, or coordinates to the two C=C double bond π -electrons, but not forming a π bond from *d* orbitals.

X-ray analysis is the best technique for the characterization of crystallizable organocalcium compounds. The ⁴³Ca NMR is rarely used because it does not provide interesting information about the structures. But, ¹³C nucleus highly enriched from calcium bonding shows especially a deshielded NMR window around 190 ppm for the *ipso* carbon nucleus. The ¹³C and ¹H NMR data constitute an interesting tool that contributes to the structure elucidation of organocalcium compounds, especially for the *non*-crystalized compounds.

Reactivity, chemical behaviour and ¹³C NMR chemical shift values of organocalcium complexes exhibit more similarities to the organolithium rather than organomagnesium derivatives, explained on the basis of their comparable electronegativity values.

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“The book ‘The Synthetic Methods, Structures, and Properties of the Ca-C σ Bond Organocalcium Containing Compounds’, by Dr Nejib Mekni and Prof Nouredine Raouafi, is a well-reviewed book and seems to be one of the rare investigations in the field. The book can be really a good reference for calcium element in general and organocalcium Ca-C σ -bond containing compounds in particular. It covers the synthetic methods, structures and properties of these derivatives, which is of special interest for the readers in the field

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