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Review

Heavy Grignard reagents—Synthesis and reactivity of organocalcium compounds

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Contents

Abstract

First investigations regarding the organic chemistry of the heavy alkaline earth metals calcium, strontium, and barium date back more than 100 years. However, challenges in the organocalcium chemistry concern the discrepancy between the unreactive metal itself and the extremely large reactivity of organocalcium compounds. Therefore, the metal has to be activated prior to use via co-condensation of the metal vapour with the substrate or by producing finely divided metal powders. The enormous reactivity of organocalcium compounds initiates side-reactions such as ether cleavage reactions. This fact enforces reaction procedures at very low temperatures. Quite often, the organocalcium compounds are only sparingly soluble due to a salt-like behaviour caused by ionic bonding situations. This problem can be overcome by bulky substituents at the periphery of the molecule or by coordination of Lewis bases such as ethers (e.g. THF, DME, [18]crown-6) to the metal centers. With the understanding of these challenges, many organocalcium compounds were prepared within the last years and characterized structurally. Preparative procedures include the direct synthesis of calcium with alkyl- and arylhalides, the metathesis reaction of calcium diiodides with potassium derivatives, metallation of H-acidic substrates with calcium compounds, transmetallation of mercury compounds with calcium, and reduction of alkenes with calcium. Stabilization of the carbanion and enhancement of the solubility of alkylcalcium compounds often succeeds by phenyl and trimethylsilyl groups in α-position. First applications of organocalcium compounds are also mentioned in this review.

Keywords: Alkylcalcium compounds; Arylcalcium compounds; Calcium; Grignard reagents; Organocalcium compounds

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1. Introduction: scope of the review

Considering the position of calcium in the periodic table of the elements it is fascinating to study the organic compounds of this element due to the enormous importance of the lighter homologous organomagnesium compounds [1–5]. In 1912, Grignard was awarded with the Nobel prize for the development of this compound class. On the one hand, a comparison with the organomagnesium compounds, the Grignard reagents [1–5], and the organolithium derivatives [6–14] allows the classification of the reactivity of these calcium compounds and the application in organic and organometallic procedures. On the other hand, the heavy alkaline earth metals possess intermediate positions between the alkali metals and the elements of the scandium group. The cations of the alkali, alkaline earth and group III metals are isoelectronic and show no redox activity. However, the rather large electronegativity difference of the alkali metals (which represent characteristic s-block metals) and carbon lead to highly ionic compounds which are salt-like and often sparingly soluble in common organic solvents. In contrast to these expectations, homoleptic organoyttrium derivatives such as $Y[CH(SiMe_3)_2]_3$ [15] show the metal centers in trigonal pyramidal environments. Due to a rather high Lewis acidity of the three-valent metals, bulky alkyl groups have to be employed in order to avoid aggregation. Similar observations are valid for isoelectronic $M[N(SiMe_3)_2]_3$ with M=Sc [16] and Y [17]. However, gaseous $Sc[N(SiMe_3)_2]_3$ showed a trigonal planar environment for the metal atom [18].

In contrast to the widely explored organomagnesium and organolithium compounds, the organocalcium chemistry [19–24] is still at its beginning. However, the determination of the crystal structure of polymeric and bent calcocene by Stucky and Zerger [25] led to a vast development of the alkaline earth metallocene chemistry which was already summarized in several excellent review articles [26–34]. Therefore, we limit our overview on alkyl- and arylcalcium derivatives. Recent investigations dealing with the heavier homologous silanides, germanides and stannanides are included as well. The main viewpoint focuses on the research of the last decade due to earlier review articles on this topic. An overview on the alkaline earth metal bis(amides) and bis(phosphanides) was published earlier, too [35,36], and therefore we restrict this report on molecules with calcium–carbon bonds. The main focus of this article is the presentation of recent results on organocalcium chemistry including challenges during preparation, preparative concepts, bonding situations, quantum chemical investigations and molecular structures.

2. Calcium hydrides

The hydrides of the heavy alkaline earth metals calcium, strontium and barium are well-known binary compounds which are the simplest compounds of these metals. Due to this fact, quantum chemical investigations were performed in order to determine the importance of d-orbital participation for the bonding situation. Furthermore, recent developments on the synthesis of molecular hydrides of calcium revived the interest in these compounds. In addition, novel fields of application of CaH_2 such as hydrogen storage materials for fuel cells [37] support the growing interest in these hydrides.

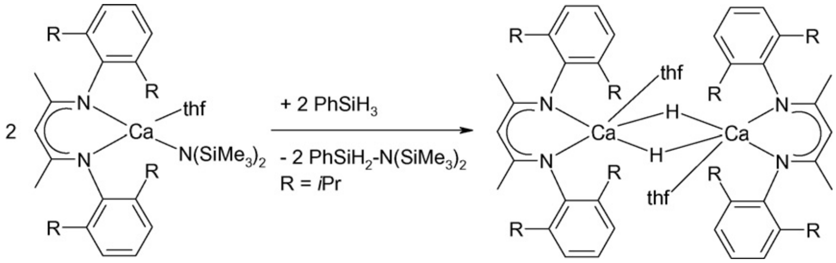
2.1. Synthesis and structures of hydridocalcium derivatives

Distilled alkaline earth metals absorb hydrogen above 400 °C (calcium and strontium) and 200 °C (barium) and form the alkaline earth metal dihydrides MH_2 according to Eq. (1) [38]. In order to obtain quantitative yields the hydrogenation temperature has to be raised to 1000 °C during the preparation. A similar procedure allowed the synthesis of high-purity calcium dihydride [39].

$$M + H_2 \xrightarrow{200-1000\,^{\circ}C} MH_2, \quad M = Ca, Sr, Ba \tag{1}$$

The crystal structure of calcium hydride and deuteride was determined very recently with high accuracy. The neutron diffraction studies of CaD_2 showed nine-coordinate calcium atoms with Ca–D distances ranging from 224.77(7) to 263.07(9) pm [40]. The two crystallographically different deuterium atoms are surrounded by four and five calcium atoms. Calcium hydride shows a first-order phase transition at 15 GPa [41]. In this high-pressure modification, the calcium atoms are surrounded by three close (Ca–H 204.5, 231.5 and 235.0 pm) and six second nearest hydrogen atoms, each H atom is surrounded by five metal atoms.

Molecules with Ca–H bonds were reported for arylcalcium hydride and are discussed in a later chapter together with other arylcalcium compounds. Nevertheless, the substitution of a bis(trimethylsilyl)amido ligand by a hydride anion succeeded smoothly with phenylsilane and yielded the structurally characterized hydridocalcium complex shown in Eq. (2) [42,43]. This centrosymmetric molecule crystallized in two different modifications depending on the solvent. From hexane solvent-free crystals were obtained (average Ca–H 215(3) pm [42]) whereas crystallization from benzene gave a solid which contained benzene molecules intercalated between the calcium complexes (average Ca–H 218(4) pm [43]).



(2)

2.2. *Quantum chemical investigations*

The alkaline earth metal hydrides attracted the interest of theoreticians for many years because numerous derivatives of the heavy alkaline earth metals such as the fluorides are bent molecules [44]. In general, compounds with metals of d^0 configuration often show unexpected molecular structures and, hence, attract attention by many research groups [45].

Possibilities to explain bent structures of molecules of the type AB_2 include (i) d-orbital participation at the metal center A, (ii) core polarization of the metal core by the anionic ligands B and (iii) van-der-Waals attraction between soft ligands B. Already in 1966, Hayes [46] suggested that the reason for the bending of AB_2 molecules is the participation of d-orbitals at the metal. DeKock et al. [47] also concluded from the bent geometries that the metal $(n-1)$d orbitals are more important than the np orbitals. In contrast to this opinion, Guido and Gigli [48] saw the cause mainly in core polarization effects. Today it is accepted that all of these factors are important in order to describe the molecular structures. The pseudopotential approach of Kaupp et al. [49] suggested linear CaH_2 whereas SrH_2 and BaH_2 were bent whereas Gillespie et al. [50] predicted a bent CaH_2 molecule. Koput [51] estimated the potential energy surface of CaH_2 with ab initio methods and found that this molecule should be bent (H–Ca–H 164.37°) with Ca–H bond lengths of 204.52 pm. However, the contour diagram showed an extremely shallow and broad potential and a very small barrier for the linearization of the molecule. Consideration of relativistic effects led to a reduction of the s–d hybridization due to stabilization of the s-orbital leading to linear CaH_2 with Ca–H bond lengths of 206.0 pm and to bent structures of SrH_2, BaH_2 and RaH_2 with bond angles of 134.6°, 117.3° and 111.7°, respectively [52].

The effects discussed for monomeric MH_2 of the heavy alkaline earth metals are also responsible for uncommon structures for the dimeric hydrides M_2H_4 [53]. Whereas the lighter congeners Be_2H_4, Mg_2H_4 and Ca_2H_4 showed molecular structures of the type $HM(\mu\text{-}H)_2MH$, the heavier derivatives Sr_2H_4 and Ba_2H_4 adopted C_{3v} symmetric structures of the type $HM(\mu\text{-}H)_3M$ with three bridging hydride anions. For these latter compounds the planar D_{2h} symmetric $HM(\mu\text{-}H)_2MH$ structure was not even a minimum on the potential energy surface but the heavy alkaline earth metal atoms showed a significant pyramidalization of the coordination sphere and a reduction to C_{2h} symmetric molecular structures.

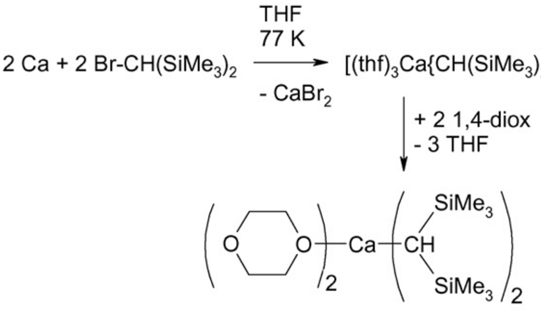
3. Alkylcalcium compounds

The substitution of hydrogen by methyl groups yields dimethylcalcium, -strontium and -barium which were studied at the Hartree-Fock level using quasirelativistic pseudopotentials [54]. Monomeric dimethylcalcium again is linear and shows a very shallow and broad energy potential with Ca–C bond lengths of 248.8 pm. Dimethylstrontium and -barium exhibit bent structures with bond angles of 130.6° and 115.9°, respectively. However, the linear molecular structure is only 1.77 and 7.83 kcal mol^{-1} higher in energy.

The preparation of alkylcalcium compounds (as well as of the heavier congeners) poses several challenges. Due to the low reactivity of the metal, activation is necessary prior to use. However, the organometallic compounds show a high reactivity and handling under anaerob conditions (strict exclusion of moisture and air) is mandatory. Isolated organocalcium compounds may inflame spontaneously. Common degradation reactions include cleavage of ether solvents which will be discussed in detail in a later chapter. Often these highly ionic organometallic compounds are also only sparingly soluble in common organic solvents and several concepts are employed to raise the solubility. Aggregation of these organic alkaline earth metallic compounds can be hindered by shielding of the Lewis acidic metal center via bulky groups at the periphery or via coordination of Lewis bases such as THF.

3.1. *Silyl and phenyl substituted methylcalcium derivatives*

Trialkylsilyl and phenyl groups in α-position stabilize carbanions and reduce the nucleophilicity due to negative hyperconjugation and mesomeric effects. The cocondensation reaction of calcium with bromo-bis(trimethylsilyl)methane in THF at 77 K yielded tris(THF)calcium bis[bis(trimethylsilyl) methanide] which presumingly formed via a Schlenk equilibrium from the insertion product $(Me_3Si)_2CH–Ca–Br$. After addition of 1,4-dioxane, the bis(1,4-dioxane) complex formed as depicted in Eq. (3). The calcium center is in a distorted tetrahedral environment with Ca–C and Ca–O bond lengths of 248.3(5) and 237.3(4) pm, respectively. The considerable anionic character of the methyne proton is shown by a high field shifted resonance at $\delta = -1.74$ in the ^1H NMR spectrum [55].



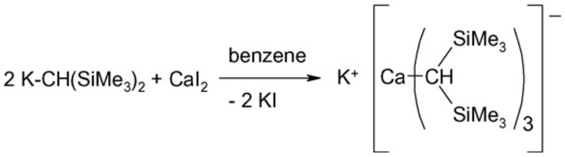
(3)

The metathesis reaction of CaI_2 with a suspension of potassium bis(trimethylsilyl)methanide in benzene yielded $K[Ca\{CH(SiMe_3)_2\}_3]$ according to Eq. (4), irrespective of stoichiometry [56]. The calciate anion $[Ca\{CH(SiMe_3)_2\}_3]^-$ which is isoelectronic to neutral $[Sc\{CH(SiMe_3)_2\}_3]$ shows an unexpected trigonal pyramidal environment for the calcium atom with C–Ca–C bond angles between 107.9(1)° and 116.1(1)° and Ca–C bond lengths from 247.4(4) to 255.6(4) pm. The ytterbiate anion adopts a similar structure [56]. A similar alkaline earth metallate was obtained earlier from this research group via the metathesis reaction of $KCH(SiMe_3)_2$ with $Ca[OS(O)_2\text{-}C_6H_4\text{-}4\text{-}Me]_2$ yielding $(thf)_3KM[CH(SiMe_3)_2]_3$ with M=Ca, Sr, Ba [57].

Table 1
M—C and M—O bond lengths (in pm) in selected benzyl derivatives of the heavy alkaline earth metals (see Eq. (7) for assignment of M, R, R′, R″, R‴, and nL)

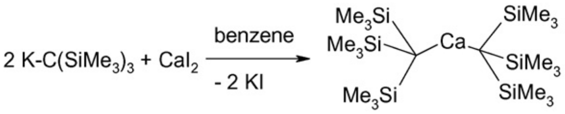
M	R	R′	R″	R‴	nL	M—C	M—O	Literature
Ca	H	H	H	H	4THF	258.1	239.8	[62]
Ca	H	H	H	*t*Bu	4THF	259.7	238.8	[62]
Ca	$SiMe_3$	H	NMe_2	H	2THF	262.8	240.7	[63]
Ca	PPh_2[a]	H	O^-	H	1THF	259.1	238.7	[64]
Ca	$SiMe_3$	$SiMe_3$	H	H	2THF	264.9		[65]
Ba	Ph	H	H	H	[18]Crown-6	308.1	277.8	[66]

[a] Compound crystallizes as a tetramer.



(4)

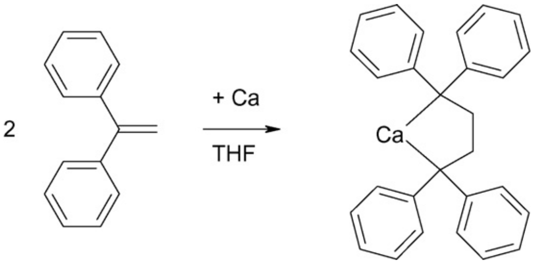
In contrast to this finding, the metathesis reaction of the extremely bulky potassium tris(trimethylsilyl)methanide with calcium diiodide in benzene afforded solvent-free colorless $Ca\{C(SiMe_3)_3\}_2$ with a bent C–Ca–C fragment of 149.7(6)° and Ca–C bond lengths of 245.9(9) pm according to Eq. (5) [58]. High level ab initio calculations showed that dimethylcalcium is a quasilinear molecule. Therefore, packing of the molecules in the solid state as well as agostic interactions between the calcium cation and methyl groups could lead to this bent C–Ca–C unit.



(5)

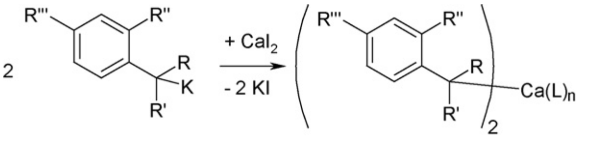
The larger alkaline earth metals strontium and barium prefer larger coordination numbers. Therefore, one of the methyl groups was substituted by a methoxy group and $(thf)Sr[C(SiMe_3)_2(SiMe_2OMe)]_2$ (Sr–C 278.6(3) and 284.9(3) pm, C–Sr–C 144.92(8)°) as well as $(dme)Ba[C(SiMe_3)_2(SiMe_2OMe)]_2$ (Ba–C 304.9(2) and 303.6(2) pm, C–Ba–C 139.89(6)°) were isolated [59].

The reduction of 1,1-diphenylethene with calcium in THF yielded calcium 1,1,4,4-tetraphenylbutane-1,4-diide according to Eq. (6) [60]. The electrolytic formation of calcium 1,1,4,4-tetraphenylbutane-1,4-diide succeeded in hexamethylphosphortriamide (HMPA) with calcium diiodide as electrolyte [61]. In this procedure, iodide was oxidized at the anode to the free halogen.



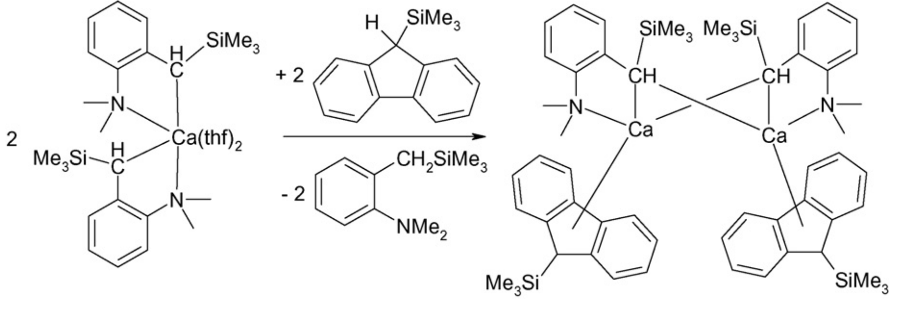
(6)

Phenyl substituents in general are able to stabilize anionic charge in an α-position, giving benzylcalcium compounds. Dibenzylcalcium was prepared via the metathesis reaction of *in situ* generated benzylpotassium and calcium diiodide in THF at −78 °C according to Eq. (7). In Table 1 an overview on benzylcalcium derivatives is given. For $(thf)_4CaBz_2$ (Bz = CH_2Ph, benzyl) a cis arrangement of the benzyl substituents was observed whereas the *tert*-butyl groups in *para*-position led to a *trans*-arrangement of the benzyl ligands [62]. In both of these compounds the alkaline earth metal atoms are in octahedral environments. In $(thf)_2Ca[CH(SiMe_3)C_6H_4\text{-}2\text{-}NMe_2]_2$ the octahedral coordination sphere of the calcium atom is strongly distorted due to the bidentate binding mode of the ligand [63]. Increasing silyl substitution as in $(thf)_2Ca[C(SiMe_3)_2Ph]_2$ [65] led to an elongation of the Ca–C bonds due to steric reasons, reduced anionic charge at the methylene fragment of the benzyl unit (hyperconjugative and delocalization effects) as well as side-on coordination of the calcium atom to the methylene, *ipso*- and *ortho*-carbon atoms. In unsubstituted benzyl anions short C–C bonds between the methylene and *ipso*-carbon atoms of 142.4 pm were observed [62] whereas in $(thf)_2Ca[C(SiMe_3)_2Ph]_2$ a bond length of 148.4 pm was found [65] due to reduced delocalization of the anionic charge into the phenyl ring and a strong hyperconjugation of the charge from a p-orbital at the carbon atom into the σ*(Si–C) orbital of the trimethylsilyl group.



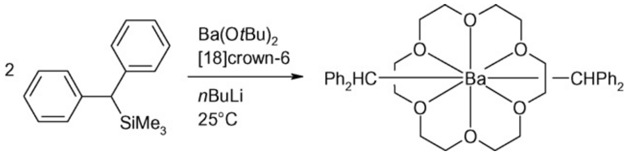
(7)

Heteroleptic benzylcalcium compounds were prepared via the metallation of trimethylsilylfluorene with $(thf)_2Ca[CH(SiMe_3)C_6H_4\text{-}2\text{-}NMe_2]_2$ (Eq. (8)) or via the disproportionation of $(thf)_2Ca[CH(SiMe_3)C_6H_4\text{-}2\text{-}NMe_2]_2$ with $Ca(C_5Me_4Et)_2$ [67]. In both cases dimeric molecules were isolated with the methylene moieties of the benzyl ligands in a bridging position between the calcium atoms.



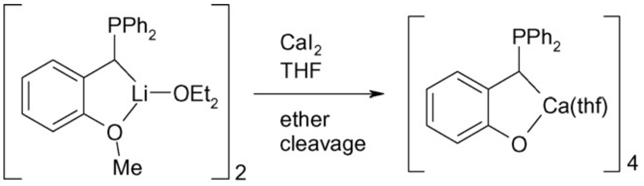
(8)

Diphenylmethyl derivatives of calcium were prepared via the transmetallation of bis(diphenylmethyl)mercury with calcium [68] or via metallation of diphenylmethane with diphenylcalcium prepared from calcium and diphenylmercury [69]. Structurally characterized derivatives were reported by Alexander and Ruhlandt-Senge [66] 30 years later. They prepared ([18]crown-6)Ba$(CHPh_2)_2$ via the reaction of diphenyl-(trimethylsilyl)methane with Ba(O*t*Bu)$_2$ in the presence of butyllithium according to Eq. (9), however, the mechanism of this reaction remained uncertain. Concentration of this reaction solution led to ether cleavage reactions and the formation of ethenolates. The triphenylmethanides of strontium [70] and barium [71] can be obtained by metallation of triphenylmethane with dibenzylstrontium and -barium, respectively. The use of $M[N(SiMe_3)_2]_2$ led to the cleavage of [18]crown-6.



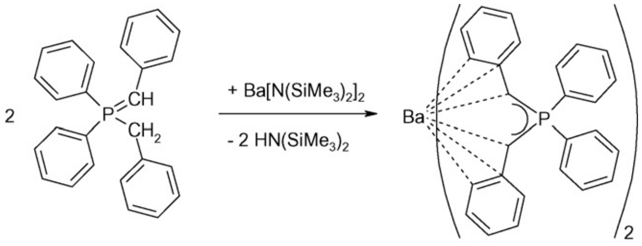
(9)

Phosphanyl substituted benzyl derivatives were reported by Knapp and Müller [64]. (2-Methoxybenzyl)diphenylphosphane was deprotonated with *n*-butyllithium and thereafter, the metathesis reaction with CaI_2 was also accompanied by an ether cleavage reaction and a tetrameric calcium complex was obtained with a rather poor yield of 12% according to Eq. (10).



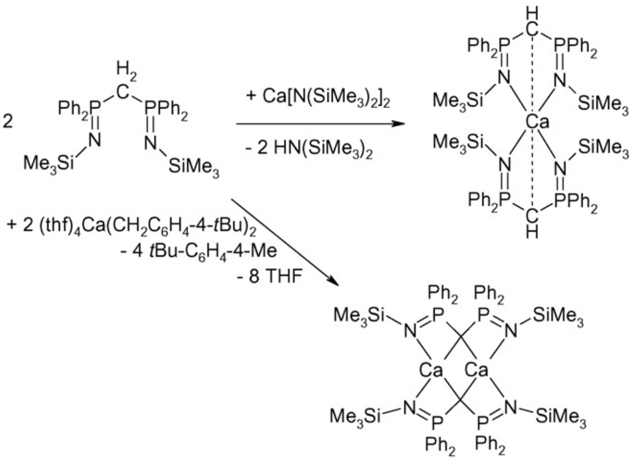
(10)

In this tetranuclear calcium complex the central structural unit consists of a Ca_4O_4 heterocubane cage with the metal atoms in strongly distorted octahedral environments with Ca–C and Ca–P bond lengths of 259.1(5) and 298.5(2) pm, respectively [64]. A barium derivative was accessible via the metallation of benzylidene-benzyl-diphenylphosporane with $Ba[N(SiMe_3)_2]_2$ according to Eq. (11) [72]. The barium atom binds side-on to the benzyl fragments with Ba–C distances in the range from 298.1(6) to 303.1(6) pm with the shortest Ba–C bonds to the *ipso*-carbon atoms.



(11)

Bis(iminophoranyl)methane can easily be deprotonated twice by butyllithium [73,74]. The mild metallation reagent $Ca[N(SiMe_3)_2]_2$ was also able to form the mono-anion irrespective of stoichiometry, whereas the reaction of $(thf)_4Ca(CH_2C_6H_4\text{-}4\text{-}t\mathrm{Bu})_2$ with $H_2C[P(Ph_2)=NSiMe_3]_2$ yielded the corresponding methanediide with a yield of 84% (Eq. (12)); this compound crystallized as a dimer [75].



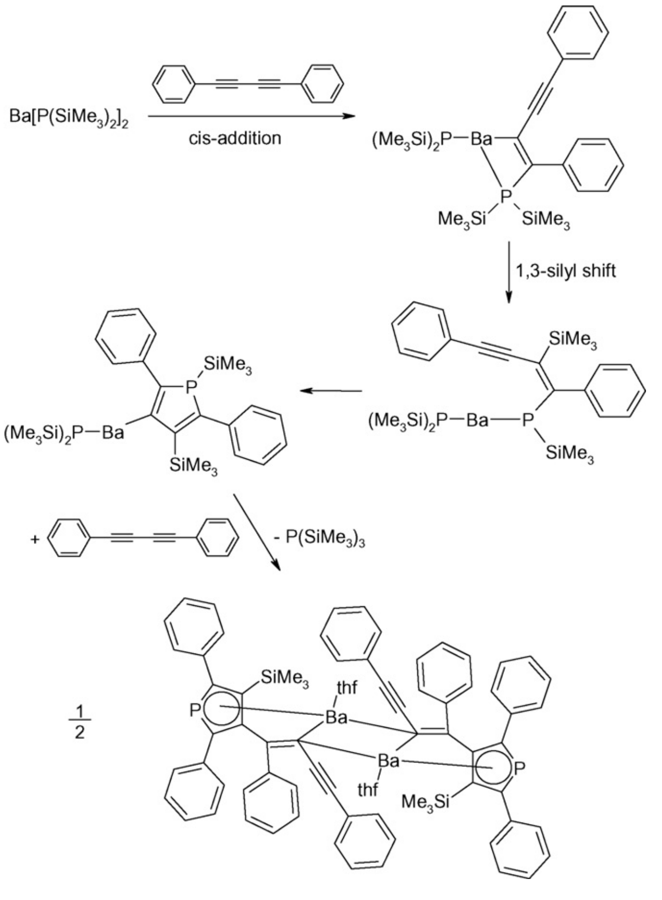
(12)

Heteroleptic $[Me_3SiN=P(Ph_2)]_2CH\text{-}Ca(thf)I$ [76] and $Ca\{CH[P(Ph_2)=NSiMe_3]_2\}_2$ [75] show large Ca–C distances of 273.5(6) and 276.5(1) pm, respectively, whereas the dimer $\{CaC[P(Ph_2)=NSiMe_3]_2\}_2$ with the central Ca_2C_2 ring displays considerably shorter calcium–carbon bonds of 255.1(3) pm. The latter methanediide was soluble in THF and benzene; addition of benzophenone led to the coordination to only one calcium atom [75]. However, neither a second keton was added nor addition of the bis(iminophosphoranyl)methanediide ligand was observed.

The reaction of calcium diisopropanolate with triethylalane yielded $CaEt_2{\cdot}0.67Al(O\mathit{i}Pr)_3$. Heating of this complex in toluene and concentration in vacuo gave $CaEt_2{\cdot}0.32Al(O\mathit{i}Pr)_3$ [77]. A recent report on the reaction of calcium alkoxides with trimethylalane in toluene showed that $AlMe_3$ coordinates to an alkoxy-oxygen atom. However, Sobota and coworkers [78] observed no ligand exchange reaction but the methyl groups could act as bridging ligands between calcium and aluminium thus forming Ca–C–Al three-center two-electron bonds. Similar bonding situations were observed for the addition products of triethylgallane to calcium and strontium bis[bis(trimethylsilyl)amide], respectively [79,80].

3.2. Alkenyl and alkynyl calcium compounds

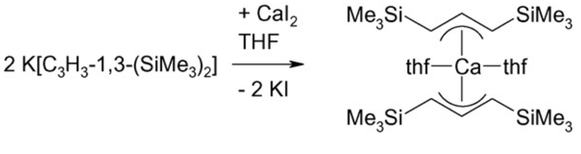
In contrast to the development of alkylcalcium compounds the investigations regarding unsaturated derivatives are rather uncommon. Nevertheless, the transmetallation of tetravinyllead [81] as well as tetraallyltin [82] and diallylmercury [83] with the heavy alkaline earth metals was reported more than 30 years ago. Recent procedures involved the reaction of barium bis[bis(trimethylsilyl)phosphanide] with diphenylbutadiyne according to Eq. (13) [84].



(13)

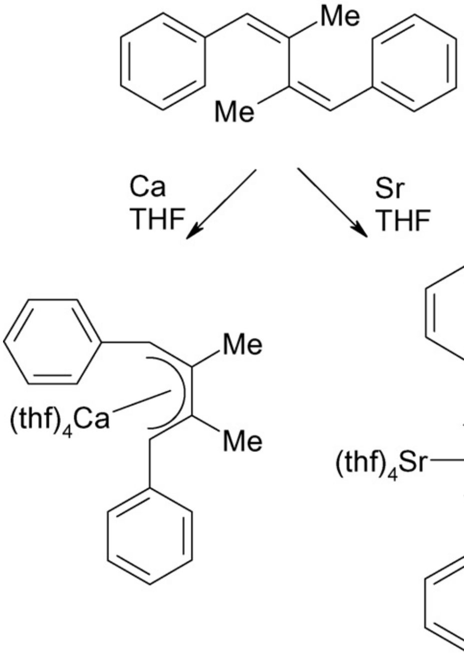
The first reaction step was a *cis*-addition of the Ba–P bond to a C≡C triple bond, followed by a 1,3-trimethylsilyl shift from the phosphorus atom to the carbon atom. The remaining Ba–P bond added to the other alkyne unit, yielding a phospholide ring. Another equivalent of diphenylbutadiyne inserted into the barium–carbon bond and finally, dimerization gave the product. The Ba–C bond to the vinyl moiety shows a similar value of 307.1(5) pm than the barium-carbon distances to the phospholide fragments with a wide variation from 289.9(5) to 336.8(5) pm owing to steric reasons [84]. The alkyne moieties show a side-on coordination to the barium atoms with Ba–C distances of 300.3(6) and 336.3(6) pm. The remaining coordination gap is occupied by a THF molecule with a Ba–O bond length of 275.8(4) pm.

The tendency of the heavy alkaline earth metals to form side-on coordination to soft π-systems rather than to build M–C σ-bonds was also expressed in allyl derivatives. The reaction of 1,2-bis(trimethylsilyl)allyl potassium with CaI_2 in THF yielded $(thf)_2Ca[C_3H_3\text{-}1,3\text{-}(SiMe_3)_2]_2$ according to Eq. (14) [85]. The Ca–C bond lengths displayed values of 265.2(3), 264.8(3) and 266.2(3) pm.



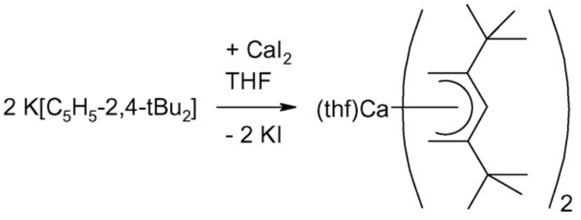
(14)

The reduction of 2,3-dimethyl-1,4-diphenylbutadiene with calcium and strontium produced the corresponding 2,3-dimethyl-1,4-diphenylbut-2-ene-1,4-diide as shown in Eq. (15) [86]. However, these alkaline earth metal derivatives showed different isomers in the solid state. Due to a higher charge in 1,4-positions, the Ca–C distances to these carbon atoms are smaller (257.4(7) and 258.8(7) pm) than to the 2,3-C atoms (274.6(7) and 277.7(7) pm) [86]. Similar observations were also valid for the strontium derivative.



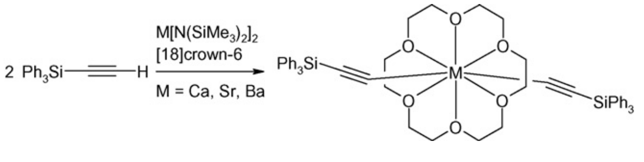
(15)

The metathesis reaction was a suitable procedure for the preparation of pentadienyl compounds of calcium (Eq. (16)). However, the reaction of $K[C_5H_5\text{-}2,4\text{-}tBu_2]$ with calcium diiodide also yielded the dimerized ligand as a by-product which was interpreted as the product of a radical reaction accompanying the metathesis reaction [87]. The Ca–C distances varied between 274(2) and 281(2) pm. The molecular structure of this “open calcocene” is comparable to those of the metallocenes of the heavy alkaline earth metals [88].



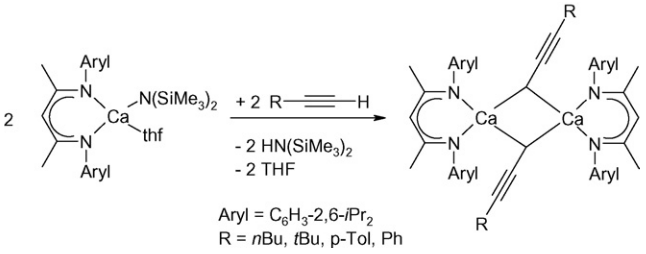
(16)

Alkynyl compounds of the heavy alkaline earth metals represent a substance class which is under investigation since many decades. As early as 1945, Gilman and Woods [89] investigated the reactivity of the bis(phenylethynyl)alkaline earth metals toward benzonitrile. They prepared these compounds via metallation of phenylacetylene with $MEt_2 \cdot ZnEt_2$ (M=Ca, Sr, Ba). Coles and Hart [90] synthesized these derivatives by adding phenylacetylene to a solution of the heavy alkaline earth metals in liquid ammonia. Treatment of triphenylsilylacetylene with $M[N(SiMe_3)_2]_2$ in the presence of [18]crown-6 gave the corresponding acetylides of calcium, strontium and barium as shown in Eq. (17) [91]. The C–M–C fragments are bent: C–Ca–C 168.7(2)°, C–Sr–C 166.0(1)°, C–Ba–C 162.7(1)° [91]. Also the M–C≡C units are bent and the barium compound shows extremely small angles of 126.6(3)° and 141.3(3)°. The average Ca–C, Sr–C and Ba–C bond lengths adopt characteristic average values of 254.1, 270.8 and 285.3 pm, respectively.



(17)

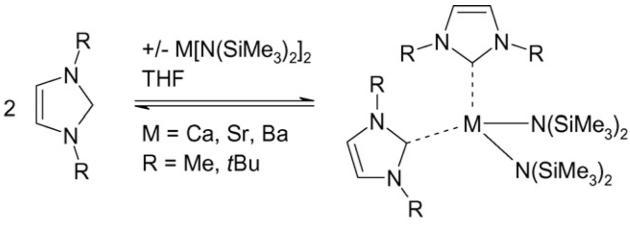
A similar procedure was employed in order to prepare heteroleptic acetylides of calcium compounds. Burkey and Hanusa [92] prepared $[(iPr_4C_5H)Ca(thf)(\mu\text{–}C{\equiv}CPh)]_2$ (Ca–C 252.1(7) and 255.1(8) pm) from the heteroleptic bis(trimethylsilyl)amide, whereas Avent et al. [93] used a bulky β-diketiminato ligand L in order to raise the solubility of $[LCa(\mu\text{-}C{\equiv}CR)]_2$ with R=*n*Bu, *t*Bu (Ca–C 249.6(2) and 251.0(1) pm), *p*-Tol (Ca–C 249.2(2) and 253.0(2) pm), Ph (Ca–C 250.5(2) and 253.5(2) pm) in hydrocarbon solvents (Eq. (18)). In the solid state, the Ca–C–C angles differ drastically for the aryl-substituted acetylides, e.g. for the bridging phenylacetylide Ca–C–C and Ca′–C–C bond angles of 172.9(1)° and 96.7(1)° are observed [93].



(18)

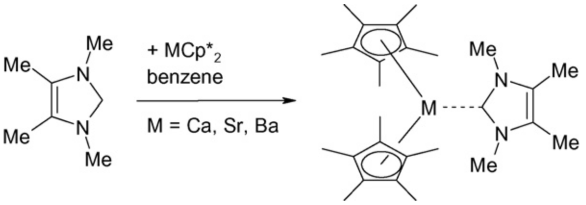
3.3. Carbene complexes of heavy alkaline earth metals

Carbene complexes are expected to form rather weak complexes because the electropositive alkaline earth metals are unable to form a significant back bonding to the carbon atom. Therefore, the carbenes act as pure σ-donors and the carbene complexes of the alkaline earth metal bis[bis(trimethylsilyl)amides] dissociated in solution according to Eq. (19) [94].



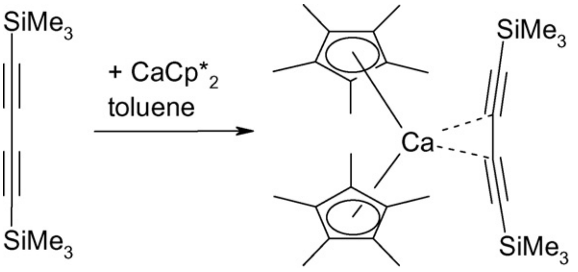
(19)

Arduengo et al. [95] investigated the coordination behaviour of tetramethylimidazol-2-ylidene towards decamethylmetallocenes. This carbene readily formed adducts with decamethylmagnesocene, -calcocene, -strontocene and -barocene according to Eq. (20). The M–C distances to the carbene ligand showed values of 219.4(2) pm for Mg, 256.2(2) pm for Ca, and 295.1(3) pm for Ba. The solid state structure of the strontocene derivative showed that two carbene molecules were bound to the alkaline earth metal (Sr–C 286.8(5) and 285.4(5) pm).



(20)

Not only carbenes can be bonded into the coordination gap of decamethylcalcocene but also butadiynes. Bis(trimethylsilyl)butadiyne formed an orange-yellow complex with $CaCp_2{}^*$ as shown in Eq. (21) [96]. Two independent molecules were found in the elementary cell with Ca–C bond lengths to the butadiyne unit of 299.1(5) and 302.4(5) pm for one molecule as well as 287.8(5) and 310.4(5) pm for the other. These large distances and the nearly unaffected bonding situation in the butadiyne fragment support an only weak coordination of this organic ligand to calcium.



(21)

3.4. Silanides, germanides and stannanides of calcium

In contrast to the vast development of organic chemistry of the heavy alkaline earth metals, there are only very few reports on the heavier homologous silanides, germanides and stannanides.

The silanides [97] and germanides [98] of the heavy alkaline earth metals were prepared via the metathesis reaction according to Eq. (22). However, THF solutions of these compounds decomposed slowly under formation of $E(SiMe_3)_4$ and elemental silicon or germanium.

$$2\ KE(SiMe_3)_3 \xrightarrow[-\ 2\ KI]{+\ MI_2,\ THF} (thf)_nM{\cdot}[E(SiMe_3)_3]_2$$

M/n = Ca/3, Sr/3, Ba/4
E = Si, Ge

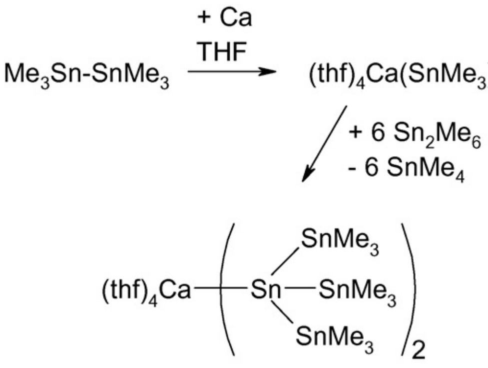
(22)

Table 2
Average M—E and M—O distances (in pm) of compounds of the general type $(L)_nM(ER_3)_2$

M	E	R	nL	M—E	M—O	Literature
Ca	C	$SiMe_3$	–	245.9	–	[58]
Ca	Si	$SiMe_3$	3THF	306.4	236.4	[97]
Ca	Ge	$SiMe_3$	3THF	304.5	237.5	[98]
Ca	Sn	Me	4THF	327.2	237.9	[99]
Sr	C	$SiMe_2R'$	1THF	281.8	252.4	[59]
Sr	Si	$SiMe_3$	3THF	319.6	252.0	[97]
Sr	Ge	$SiMe_3$	3THF	317.3	251.9	[98]
Ba	C	$SiMe_2R'$	DME	304.3	277.6	[59]
Ba	Si	$SiMe_3$	4THF	344.1	273.5	[97,100]
Ba	Ge	$SiMe_3$	4THF	341.5	273.5	[98]

Selected structural parameters are listed in Table 2. The most striking feature concerns the M–E bonds: the alkaline earth metal–silicon bonds are slightly longer than the metal–germanium bonds. This oberservation was explained by Teng and Ruhlandt-Senge [97,98] by increased polar character in the alkaline earth metal–germanium bond due to a larger electronegativity of Ge.

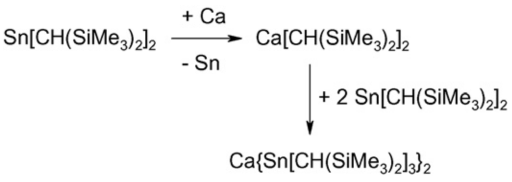
Tetrakis(tetrahydrofuran)calcium bis(trimethylstannanide) was prepared in THF via the insertion of calcium into the Sn–Sn bond of hexamethyldistannane [99]. This compound reacted with additional hexamethyldistannane and underwent degradation via migration of trimethylstannyl groups. In Eq. (23) the reaction is summarized, the stoichiometry was checked experimentally.



(23)

The triphenylstannanides of the heavy alkaline earth metals formed solvent-separated ions [101]. These compounds also decomposed under reduction and group migration, yielding $M[Sn(SnPh_3)_3]_2$, $Sn(SnPh_3)_4$, $SnPh_4$, and elemental tin. The tendency to decompose increased from silicon to tin which is in agreement with decreasing bond strengths and increasing ionic M–E bond character.

The transmetallation of $Sn[N(SiMe_3)_2]_2$ with the alkaline earth metals yielded quantitatively $M[N(SiMe_3)_2]_2$ with M=Ca, Sr, Ba [102,103], the formation of heterobimetallic compounds which contain tin and the alkaline earth metals were not observed. However, a reaction of isoelectronic $Sn[CH(SiMe_3)_2]_2$ with calcium metal under similar conditions gave a stannanide according to Eq. (24). Resulting $Ca\{Sn[CH(SiMe_3)_2]_3\}_2$ formed via an insertion of $Sn[CH(SiMe_3)_2]_2$ into the Ca–C bonds of $Ca[CH(SiMe_3)_2]_2$ [104].



(24)

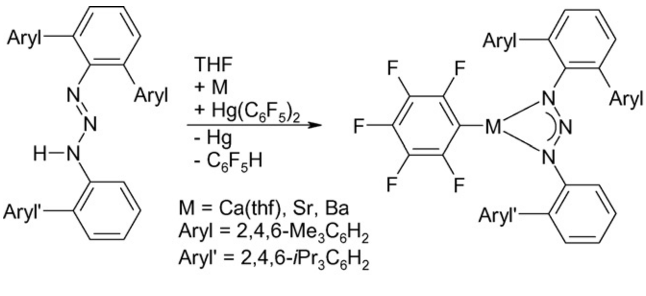
If the substituents at tin are very electronegative such as alkoxides an “inverse” coordination was observed. Examples include the reaction of $Ca(OSiMe_2tBu)_2$ with $Sn(OSiMe_2tBu)_2$ in DME yielding $Ca[(\mu\text{-}OSiMe_2tBu)_3Sn]_2$ [105]. Additional examples may be found elsewhere (see, for example [106,107]).

4. Arylcalcium compounds

The first report on the direct synthesis of phenylcalcium halide dates back to 1905 when Beckmann [108] inserted calcium into the C–I bond of iodobenzene. However, a repetition of this procedure by Gilman and Schulze [109] showed that the major product consisted of the diethylether complex of calcium diiodide. Many reports on arylcalcium compounds followed, however, these compounds remained poorly characterized. In general, derivatization reactions and hydrolytic work-up procedures were employed in order to conclude that an organocalcium compound had been prepared. Tremendous success in preparing alkyl- and benzylcalcium compounds as described in the last chapter stimulated growing interest in arylcalcium derivatives.

4.1. Synthesis and limitations

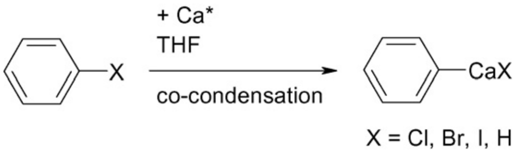
Employing the concept of bulky ligands to ensure solubility in common organic solvents and to shield the reactive Ca–C bonds led to the use of bulky triazenide substituents. As shown in Eq. (25) the pentafluorophenylcalcium, -strontium and -barium derivatives were prepared from bis(pentafluorophenyl)mercury [110]. The M–C bonds (Ca–C 250(1), Sr–C 267.3(7), Ba–C 280.8(5) pm [110]) are shielded by coordination of the alkaline earth metal atoms to the π-systems of the triazenide-aryl groups.



(25)

The transmetallation of diphenylmercury with calcium turnings in THF was reported earlier [111,112]. In a typical procedure, calcium was activated by amalgamation and then reacted with diphenylmercury in boiling THF. During this process the solution turned dark red. After cooling to room temperature and stirring for an additional hour, all solids were removed and the solution showed a yield of 97% for diphenylcalcium by acid titration.

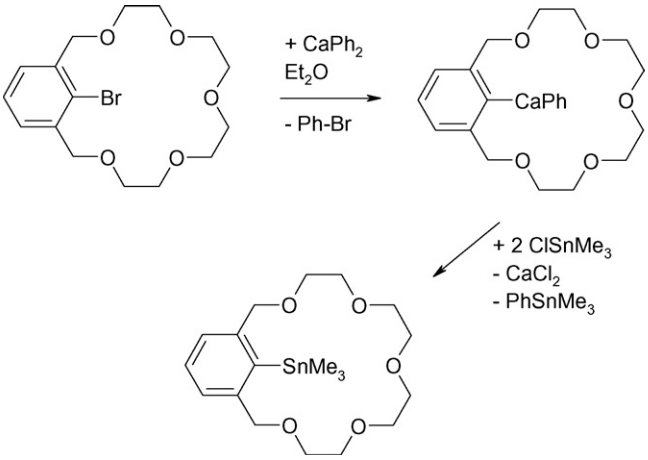
The employment of calcium metal for the preparation of organocalcium compounds affords its activation prior to use. Another possibility is the use of calcium vapour which reacts with an excess of arylhalides and is cocondensed on a cooled surface. The color of the arylcalcium halides was reddish-brown. The yield was determined after hydrolysis from the amount of arene and was 38.4% for PhCaF, 47.5% for PhCaCl and 48.8% for PhCaBr [113]. The reaction of a calcium atom-THF slurry with phenylhalides gave no reaction for fluorobenzene and a yield of 32.4% for PhCaCl, 68.7% for PhCaBr and 98.0% for PhCaI (Eq. (26)) [114], further examples are reviewed elsewhere [115]. Even an insertion of Ca atoms into a C–H bond of benzene was observed, yielding black PhCaH [116]. The black solid was dissolved in THF and a resonance at $\delta(^1H) = 0.2$ was assigned to the calcium-bound hydride, deuterolysis yielded $[D_1]$benzene. A cocondensation reaction in the presence of THF gave dark red, pyrophoric and nearly insoluble $(thf)_2Ca(Ph)H$ with a yield of 78% [117]. A strong signal at $1094\,cm^{-1}$ in the IR spectrum was assigned to the Ca–H vibration. Derivatization occurred via reaction with substituted phenols yielding calcium bis(phenolates).



(26)

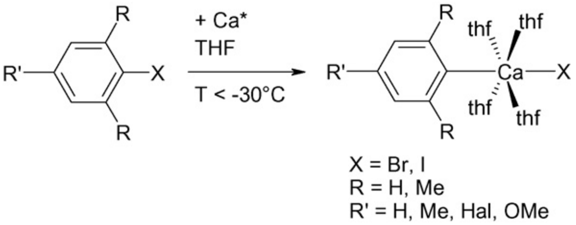
The direct synthesis in an organic solvent in order to prepare arylcalcium halides was investigated for many years. Mochida et al. [118] reacted ultrafine Ca particles with organic halides, a stabilization of RCaI by complexation with Lewis bases such as 1,4-dioxane, THF and NEt_3 was reported [119]. The direct synthesis of arylcalcium halides performed in hydrocarbons only gave poor yields [120]. The importance of impurities of the calcium metal strongly influenced the reactivity of the alkaline earth metal; traces of magnesium and sodium improved the yields of PhCaI in THF [121].

The direct synthesis of calcium with iodobenzene in THF at −20 °C, the subsequent removal of THF and dissolving in Et_2O yielded diphenylcalcium which decomposed rapidly in THF solution [122]. The reaction of diphenylcalcium with 2-bromo-1,3-xylylene-[18]crown-5 gave a calcium/halogen exchange reaction according to Eq. (27). The product was characterized via the metathesis reaction with chloro-trimethylstannane which gave 2-trimethylstannyl-1,3-xylylene-[18]crown-5, phenyl-trimethylstannane and calcium dichloride [122].



(27)

Activation of the heavy alkaline earth metals succeeds via dissolving of the metal in liquid ammonia and immediate removal of the solvent thereafter in order to avoid amide formation. These pyrophoric metal powders reacted in THF at very low temperatures with iodobenzene and substituted iodoarenes to the corresponding arylcalcium iodides as shown in Eq. (28). In *para*-position many functional groups were tolerated whereas halogen atoms in *ortho*-position initiated decomposition of these arylcalcium derivatives. Above approximately −30 °C degradation reactions via ether cleavage took place and led to the formation of side-products which are discussed in the next chapter. A general procedure is given for a synthesis at 0 °C because at this temperature the formation of heavy Grignard reagents RCaI (R = aryl) is rather fast compared to the decomposition via ether cleavage [123].



(28)

Table 3 gives an overview on arylcalcium halides. The yields strongly depended on the halogen atom X. Iodoarenes gave good yields, no reaction was observed for chloroarenes. Many functional groups were tolerated in *para*-position; 1,4-diiodobenzene only reacted once with activated calcium irrespective of the metal excess. This fact shows the reduced reactivity of calcium compared to magnesium which is able to produce $IMg–C_6H_4–4–MgI$ [127]. Lithium/iodine exchange reactions also allowed the isolation of *para*-dilithiobenzene [128]. Halogen atoms in *ortho*-position led to fast decomposition and formation of calcium dihalide. Thus, $F_5C_6–Ca–I$ was unstable in THF, however, bulky shielding groups were able to protect the $F_5C_6–Ca$ moiety (Eq. (25)) [110]. In $^{13}C\{^1H\}$ NMR experiments, arylcalcium halides show a low field shift of the *ipso*-carbon atoms. This low field shift even increases for the heavier alkaline earth metals and $\delta(^{13}C\{^1H\})$ values of 194.5 and 210 were found for PhSrI and PhBaI, respectively, in THF solutions [129]. The Ca–C and

Table 3
Yields of the direct synthesis of arylcalcium halides and characteristic data (see Eq. (27) for the assignment of R, R′ and X)

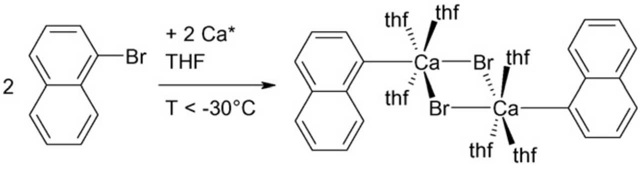
R_{ortho}	R'_{para}	X	Yield/%	$\delta(^{13}C_{ipso})$	M—C	M—O	Literature
Me	Me	I	90	182.5	257.4	240.6	[124]
OMe	H	I	56	152.0			[123]
H	H	I	93	190.3	257.4	238	[123]
H	H	Br	71	190.0	258.3	238.7	[123,125]
H	H	Cl	<5	No reaction			[123]
H	Me	I	60	185.3	255.6	238.2	[125]
H	Ph	I	<5	Fast decomposition			[123]
H	F	I	75	186.6			[123]
H	Cl	I	81	187.8			[123]
H	I	I	95	188.9			[123]
H	OMe	I	89	178.0			[123]
H	NMe_2	I	91	173.6			[123]
H	$SiPh_3$	I	85	194.5			[126]
H	$SiMe_2R''$[a]	I	56	191.2			[126]
C_6F_5	I	<5	Fast decomposition				[123]
Naphthyl		I	68	195.4	255.2	238.4	[123]

The $\delta(^{13}C_{ipso})$ NMR shifts (in ppm) were recorded at $[D_8]$THF solutions, the M—C and average M—O bond lengths (in pm) were observed at $(thf)_4Ca(Aryl)X$ with the anions in a *trans*-position.

[a] $R'' = —C_6H_4—4\text{-}Ca(thf)_4I$.

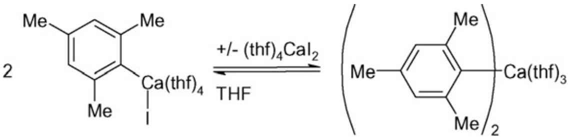
Ca–O bond lengths vary in rather narrow ranges which are characteristic for six-coordinate calcium atoms.

Naphthylcalcium iodide crystallized monomeric as a tetrakis(THF) complex with the anionic ligands in a *trans*-position [123]. However, the direct synthesis of naphthylbromide with activated calcium yielded naphthylcalcium bromide which precipitated from THF solution as a dimer with bromine atoms in a bridging position (Eq. (29)). In this dinuclear complex the calcium atoms are in distorted octahedral environments with Ca–C and Ca–O bond lengths of 252.8(4) and 240.5 pm [130]. The Ca–Br distances of 293.41(8) and 294.57(8) pm are comparable. The bromine atom shows a larger Pearson hardness and therefore, it can substitute a THF molecule in the coordination sphere of calcium, whereas the soft iodine atom obviously is unable to replace a THF ligand.



(29)

The NMR spectra of several arylcalcium iodides showed two sets of signals which can be interpreted in the sense of a Schlenk equilibrium. Eq. (30) displays this equilibrium for mesitylcalcium iodide. Repeated crystallization of $(thf)_4CaI_2$ and concentration of the mother liquor finally led to a very concentrated THF solution of 2,4,6-trimethylphenylcalcium iodide from which dimesitylcalcium crystallized at −90 °C as a tris(THF) adduct [131]. The five-coordinate calcium center shows a trigonal bipyramidal coordination sphere with the bulky mesityl anions in the equatorial plane. Due to the small coordination number a Ca–C bond length of 252.0(3) pm is observed. The extremely high solubility of diarylcalcium is striking and initiated quantum chemical calculations which showed that a η^6-coordination of aryl groups to the neighbouring calcium atom is energetically of a similar order of magnitude as the coordination of THF molecules [131].



(30)

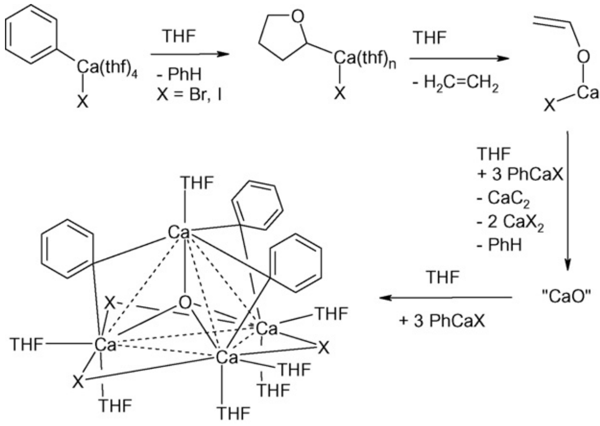
In order to decrease the solubility of arylcalcium compounds in common organic solvents two concepts seem to be applicable, namely the incorporation of large groups such as triphenylsilyl or the synthesis of multinuclear complexes. Therefore, iodo-4-triphenylsilylbenzene readily reacted with activated alkaline earth metals and gave less soluble aryl derivatives of the alkaline earth metals [126]. In order to test the other concept $Me_2Si(C_6H_4\text{-}4\text{-}I)_2$ was reacted in THF with activated calcium [126]. Dinuclear $Me_2Si[C_6H_4\text{-}4\text{-}Ca(thf)_4I]_2$ readily formed, however, ether cleavage led to impurities of $PhMe_2Si\text{-}C_6H_4\text{-}4\text{-}Ca(thf)_4I$.

4.2. Degradation in THF

Ether cleavage reactions are well known in the organic alkali metal chemistry [132]. Whereas the cleavage of THF starts with a deprotonation in α-position, the attack of carbanions at diethylether occurs preferably in a β-position. However, depending on the solvent and the bulkiness of the reagents also α-deprotonation can be observed. More than 30 years ago ether cleavage of, e.g. 1,3-benzoxathiole and 1,3-benzodioxole with organic calcium compounds such as PhCaBr was investigated [133]. A rapid decomposition of diphenylcalcium in THF solution was also observed earlier [122]. Ether cleavage occurred in THF solutions of the alkaline earth metal bis[bis(trimethysilyl)amides] as well [134].

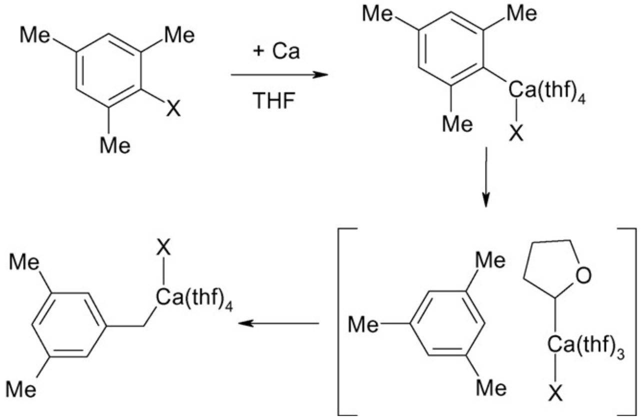
With respect to these observations it is astonishing that the transmetallation of diphenylmercury with calcium in boiling THF gave diphenylcalcium with a yield of 97% [111,112]. These compounds were identified by derivatization reactions. In order to clarify these contradictory reports, a closer look at the ether cleavage by arylcalcium compounds was undertaken.

A THF solution of arylcalcium iodide was stored at room temperature for several days in a sealed NMR tube. This procedure allowed to record NMR spectra on a regular basis without the risk of introducing moisture and air to the solution. Within several days the precipitation of colorless crystals was observed. The degradation reaction of $(thf)_4Ca(Ph)I$ in THF is represented in Eq. (31). The first step was the α-deprotonation of a THF molecule with subsequent formation of ethane and ethenolate. All three products (benzene, $H_2C{=}CH_2$ and $H_2C{=}CH{-}OCaI$) were observed in ^1H as well as $^{13}C\{^1H\}$ NMR experiments. Whereas the amount of benzene increased, the concentration of ethenolate decreased. This fact was interpreted in the sense that $(thf)_4Ca(Ph)I$ was able to deprotonate $H_2C{=}CH{-}OCaI$ completely, yielding “CaO” and presumably CaC_2. Phenylcalcium iodide trapped the formed CaO giving the cage compound $[\{(thf)_2Ca(Ph)I\}_3(thf)CaO]$ as shown in Eq. (31). After complete degradation of the ethenolate the remaining phenyl groups showed a strongly reduced tendency to cleave ether. In order to detect CaC_2, chloro-trimethylsilane was added to the reaction mixture and bis(trimethylsilyl)acetylene was identified.



(31)

A minor side reaction occurred for the degradation of mesitylcalcium iodide in THF solution according to Eq. (32). The deprotonated THF molecule reacted again with the just formed 1,3,5-trimethylbenzene giving a yellow 3,5-dimethylbenzylcalcium derivative [124].



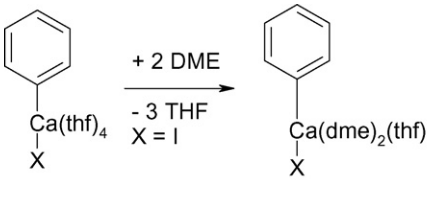
(32)

Cleavage of THF occurs already at room temperature and is common in organocalcium chemistry. Therefore, several oxygen-centered calcium cages have been isolated and characterized via crystal strucrure determinations: $[\{2,6\text{-}(MeO)_2C_6H_3\text{-}Ca\}_3\cdot CaO]$ [135], $[\{(thf)_2CaPhI\}_3\cdot(thf)CaO]$ [136], and $[\{(thf)_2CaPhBr\}_3\cdot MgO]$ [137] with oxygen-centered distorted M_4O tetrahedrons as well as $[\{(Et_2O)_2CaPh_2\}_4\cdot(Et_2O)CaO]$ [138] and $[\{(thf)_2BaPh_2\}_4\cdot(thf)BaO]$ [129] with oxygen-centered M_5O square pyramids. Nevertheless, THF proved to be the best solvent choice for the direct synthesis of arylcalcium compounds. In diethylether or hydrocarbons the yields were much lower or no reactions occurred.

4.3. Reactivity studies

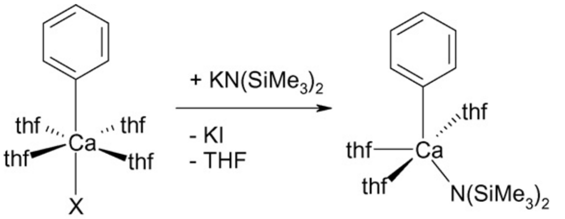
The organic lithium and magnesium compounds belong to the most widely used reagents in the organometallic chemistry. A similar importance was expected for the organocalcium chemistry already many years ago [139]. However, due to difficulties in preparing (e.g. necessity of metal activation prior to use) and handling (e.g. air and moisture sensitivity, tendency to cleave ethers) of these compounds a broad application was hindered. Nevertheless, even first catalytic applications such as hydrosilylation [140] and hydrophosphination [141] of alkenes and alkynes were reported recently. The most prominent field of applications represents the ring opening polymerization of lactides and cyclic esters (see for example [142–144]) as well as of styrene [145]. In this overview the reactivity studies are restricted to stoichiometric reactions.

The calcium/halogen exchange reaction was already shown in Eq. (27) [122]. In order to reduce the high tendency for ether cleavage reactions, a more effective shielding of the Ca–C bonds seemed feasible. Therefore, the coordination number of calcium was raised by substituting three THF molecules by two 1,2-dimethoxyethane molecules as shown in Eq. (33).



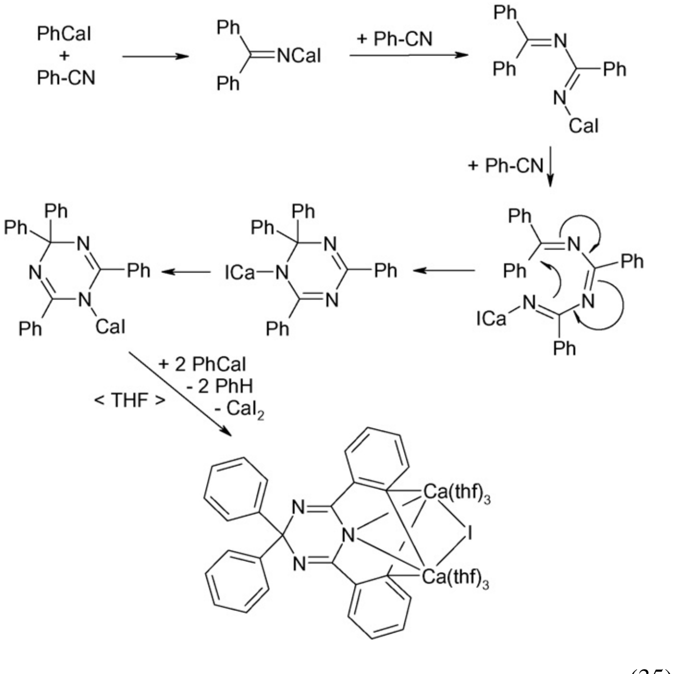
(33)

In $(dme)_2(thf)CaPhI$ the larger coordination number of calcium led to a slight elongation of the Ca–C bond (Ca–C 262.1(5) pm) [125]. Another possibility consists of replacing the iodine ligand by a more bulky anion such as $N(SiMe_3)_2$. The halide was substituted via the metathesis reaction of $(thf)_4Ca(Ph)I$ with potassium bis(trimethylsilyl)amide yielding $(thf)_3Ca(Ph)\text{-}N(SiMe_3)_2$ with Ca–C bond lengths of 253.4(3) pm (Eq. (34)) [137]. The iodine could also be exchanged against a PPh_2 group. However, the reaction of $(thf)_4Ca(Ph)I$ with KCp and KOR gave the homoleptic compounds $CaPh_2$ and $CaCp_2/Ca(OR)_2$ which resulted from the Schlenk equilibrium.



(34)

The reaction of $(thf)_4Ca(Ph)I$ with benzonitrile led to the polymerization of Ph–C≡N. However, the reaction of phenylcalcium iodide in THF with potassium *N*,*N*′-bis(trimethylsilyl)benzamidinate gave a dinuclear complex via addition and metallation reactions as proposed in Eq. (35) [137]. The key step was the very slow liberation of benzonitrile from the *N*,*N*′-bis(trimethylsilyl)benzamidinate anion. Despite the stability of calcium bis[*N*,*N*′-bis(trimethylsilyl)benzamidinate] [146], benzonitrile was liberated and the phenyl group added immediately to the C≡N triple bond. Two additional benzonitrile molecules were inserted into the Ca–C bond. Thereafter, directed *ortho* metallation led to the dinuclear product with Ca–C distances of 266.8(6) and 268.7(6) pm as shown in Eq. (34). A similar reaction mechanism was offered for the reaction of phenylsodium with benzonitrile many years ago [147,148].



(35)

Organocalcium compounds can also be used as metallation reagents. Utke and Sanderson [149] showed that calcium metal is quite unreactive towards a large variety of amines which only formed complexes with Ca^0, even if the metal was dissolved in liquid ammonia. Therefore, other procedures were developed. Activated calcium metal is not reactive enough to deprotonate aniline and diphenylamine. Therefore, the metathesis reaction of PhCaI with KN(H)Ph [150] and $KNPh_2$ [151] in THF offered access to the phenylcalcium amides which dismutated immediately to homoleptic $CaPh_2$ and $Ca(NHPh)_2$ [150] and $Ca(NPh_2)_2$ [151], respectively. Another possibility was the metallation of aniline and diphenylamine with PhCaI in THF, followed by dismutation to $(thf)_4CaI_2$ and calcium diamides [150,151].

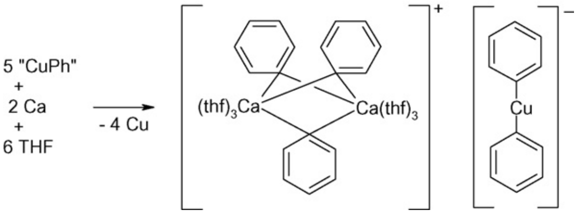
5. Heterobimetallic compounds with calcium

Heterobimetallic compounds of calcium gained on interest due to a raised reactivity compared with the homoleptic compounds and were reviewed very recently [22]. In addition, heterobimetallic compounds of magnesium and the alkali metals form “inverse crowns” and show a selection of interesting reactions as strong deprotonation reagents [152–154]. Due to these very recent reviews, the discussions of heterobimetallic compounds with calcium are limited to cuprates, zincates, and vanadates.

5.1. Organic cuprates of calcium

Organic cuprates of lithium and magnesium play an important role in organic chemistry as Gilman reagents [155] which are often formed in situ by adding catalytic amounts of copper(I) salts to the organolithium and -magnesium reagents. Despite this manifold use in chemistry, the investigations on cuprates of the heavier alkaline earth metals are very limited. The metathesis reaction of $Na_2[Cu(C{\equiv}CH)_3]$ with calcium nitrate in liquid ammonia yielded the sparingly soluble ion pair $[Ca(NH_3)_6]^{2+}$ $[Cu(C{\equiv}CH)_3]^{2-}$ [156]. The nearly trigonal planar anions show Cu–C bond lengths of 203.1(7) pm.

The transmetallation of phenylcopper(I) with calcium according to Eq. (36) gave the insoluble ion pair $[(thf)_3Ca(\mu\text{-}Ph)_3Ca(thf)_3]^+$ $[PhCuPh]^-$ [137], the cuprate anion being planar with Cu–C distances of 191.0(3) pm. A further transmetallation was not possible most probably due to the insolubility of $[(thf)_3Ca(\mu\text{-}Ph)_3Ca(thf)_3]^+$ $[PhCuPh]^-$ which also spoils the far-reaching application in organometallic chemistry.

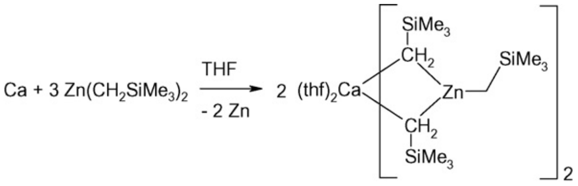


(36)

5.2. Organic zincates of the alkaline earth metals

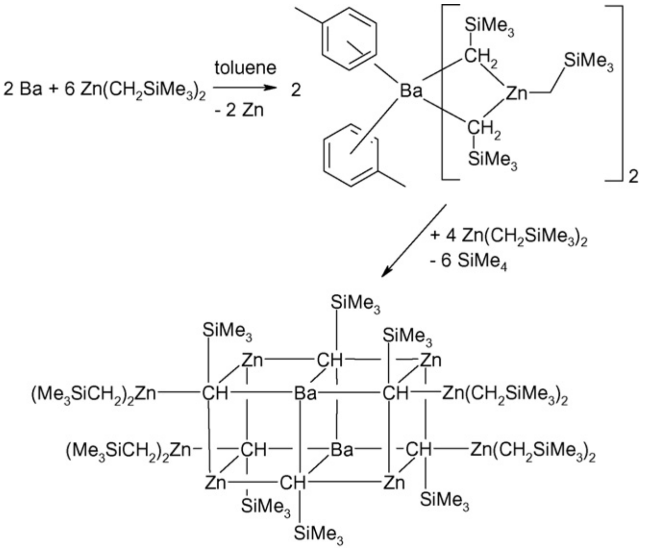
Organic alkaline earth metal zincates are substances which were studied already many years ago. Kaufmann et al. [157] investigated solution equilibria of $MZnEt_4$ with M=Ca, Sr, Ba such as the formation of solvent-separated ions $M^{2+}/ZnEt_4{}^{2-}$, contact ion pairs $MZnEt_4$ and homoleptic compounds $CaEt_2/ZnEt_2$. The reactivity of the zincates $CaZnR_4$ proved to be higher than the reactivity of either CaR_2 or ZnR_2 [158]. The reaction of distilled heavy alkaline earth metals with $Zn(CH_2SiMe_3)_2$ yielded the corresponding tris(trimethylsilylmethyl)zincates of calcium (Eq. (37)) [159], strontium and barium [160]. However, a decomposition into

$M(CH_2SiMe_3)_2$ and $Zn(CH_2SiMe_3)_2$ was neither observed by a solvent change nor at high temperatures.



(37)

Heating of barium with $Zn[CH(SiMe_3)_2]_2$ in toluene gave the bis(toluene) adduct of barium bis[tris(trimethylsilylmethyl)-zincate] [160] which yielded in the presence of excess of $Zn[CH(SiMe_3)_2]_2$ a heterobimetallic cage compound which is best described as two heterocubane cages with a common Ba_2C_2 face [161]. The reaction sequence is shown in Eq. (38). Barium bis[tris(trimethylsilylmethyl)zincate] deprotonated 2,3-bis(trimethylsilyl)-2,3-dicarba-nidohexaborane in THF yielding the expected barium bis(carborate) [162]. The also formed dialkylzinc was not able to deprotonate the carborane.

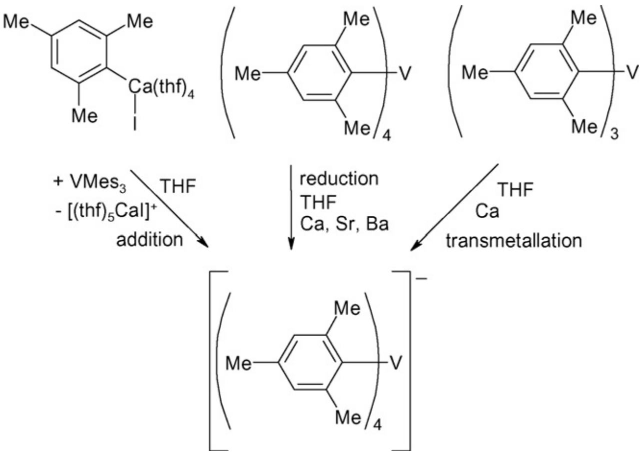


(38)

The metathesis reaction of $Ca(NO_3)_2$, $Sr(NO_3)_2$, and $Ba(SCN)_2$ with $Na_2Zn(C{\equiv}CH)_4$ in liquid ammonia yielded the corresponding amorphous alkaline earth metal tetraethynylzincates [163]. The C≡C vibration decreased from $1959\,cm^{-1}$ for the magnesium derivative over 1946 and 1947 to $1943\,cm^{-1}$ for $BaZn(C{\equiv}CH)_4$.

5.3. Organic vanadates of calcium

The transfer of aryl groups to other organometallic compounds leads to the formation of metallates. As a representative example, the vanadates(III) were investigated. $(thf)_4Ca(Mes)I$ transferred the mesityl group to $V(Mes)_3$ yielding $[(thf)_5CaI]^+$ $[V(Mes)_4]^-$ [164]. The transmetallation reaction (reaction of $V(Mes)_3$ with calcium metal) also gave tetra(mesityl)vanadate(III) anions shown in Eq. (39), the counter ion being $[(thf)_6Ca]^{2+}$. A third possibility to prepare tetra(mesityl)vanadates consisted in a reduction of $V(Mes)_4$ with calcium metal. However, the yield of this reaction was rather poor. The vanadium(III) center of the tetra(mesityl)vanadate anion is in a distorted tetrahedral environment with two small (97.8°) and four large CVC bond angles (115.6°). Similar structural parameters were found for tetramesitylvanadium(IV) with CVC angles varying from 96.4° to 117.8° [165]. The addition of organolithium compounds to trimesitylvanadium(III) also offered a general access to tetraorganylvanadates(III) [166–168].



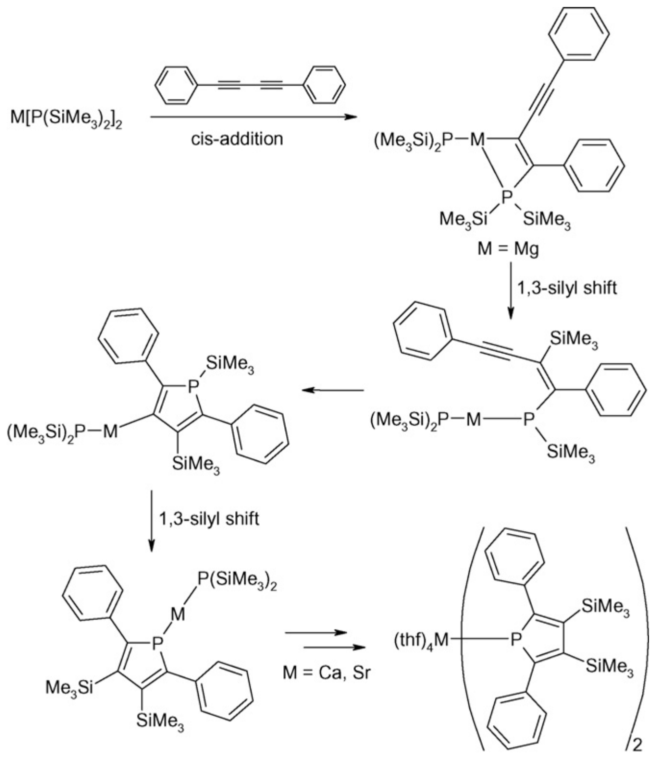
(39)

These compounds were extremely air sensitive. Seidel and Kreisel [169] showed already 30 years ago that lithium tetramesitylvanadate(III) (prepared from LiMes and $V(Mes)_3$ [170]) was oxidized by air yielding tetramesitylvanadium [169]. Trimesitylvanadium also reacted with dioxygen giving $Mes_3V\text{-}(\mu\text{-}O_2)\text{-}VMes_3$ [171] and with dinitrogen giving $Mes_3V\text{-}(\mu\text{-}N_2)\text{-}VMes_3$ [172]; under reducing conditions using Na, K or electrochemical procedures vanadate anions such as $[Mes_3V\text{-}(\mu\text{-}N_2)\text{-}VMes_3]^-$ and $[Mes_3V\text{-}(\mu\text{-}N_2)\text{-}VMes_3]^{2-}$ were formed [172].

6. Conclusion and prospective

The organocalcium chemistry is dominated by the extremely large reactivity difference of the metal on the one hand and of the arylcalcium compounds on the other. Activated calcium powder proved to be less reactive than lithium and magnesium. Thus, magnesium could react twice with 1,4-diiodobenzene yielding $IMg–C_6H_4–MgI$ whereas even in the presence of an excess of calcium only the mono-insertion product $I\text{-}C_6H_4\text{-}4\text{-}CaI$ was formed. On the other hand, the organocalcium compounds are very reactive and, therefore, easily cleave ether. This reactivity enforces reaction conditions at very low temperatures, depending on the shielding of the reactive Ca–C bonds. The reactivity of Sr and Ba is also higher than of calcium. This fact is demonstrated by the reaction of activated alkaline earth metals with amines: whereas strontium and barium deprotonate aniline and diphenylamine yielding the corresponding bis(amides), calcium is not able to metallate these amines.

The organometallic compounds itself show an increasing reactivity from magnesium to barium. Due to the fact that the organic chemistry of the heavy alkaline earth metals still stands at its beginning, an impressive example is given for the reaction of an alkaline earth metal bis[bis(trimethylsilyl)phosphanide] with diphenylbutadiyne. Barium bis[bis(trimethylsilyl)phosphanide] gives with diphenylbutadiyne the vinylbarium complex as shown in Eq. (13). The lighter alkaline earth metal bis(phosphanides) show a graded reactivity towards $Ph{-}C{\equiv}C{-}C{\equiv}C{-}Ph$: Whereas $Mg[P(SiMe_3)_2]_2$ only adds to the alkyne moiety, the calcium and strontium bis(phosphanides) form the corresponding 2,5-diphenyl-3,4-bis(trimethylsilyl)phospholides according to Eq. (40). Similar reactivity differences might be expected for aryl and alkyl derivatives of the alkaline earth metals because the phosphanides often show a strong similarity to the methanides due to the diagonal relationship in the periodic table.



(40)

The long tradition of the organic zinc [173], lithium [14,174], and magnesium chemistry [3,174] opened many fields of applications for these derivatives. Even though, first investigations regarding the organocalcium compounds were undertaken many decades ago, the understanding of the reaction behaviour and the structures afforded versatile and sophisticated methods for the synthesis and characterization of these extremely air sensitive and reactive compounds. From our investigations it can be concluded that in several earlier reports on the synthesis of arylcalcium halides oxygen-centered cages might have been obtained, especially when elevated temperatures were applied in order to maximize the yield. Common derivatization reactions such as insertion of CO_2 into the M–C bond followed by hydrolytic work-up or addition of chlorosilanes or -stannanes often are not suitable methods in order to distinguish between the heavy Grignard reagent RCaX and oxygen-centered cage compounds.

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