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Direct Synthesis of Heavy *Grignard* Reagents – Challenges, Limitations, and Derivatization

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Dedicated to Professor Dietmar Stalke on the Occasion of his 60th Birthday

Abstract

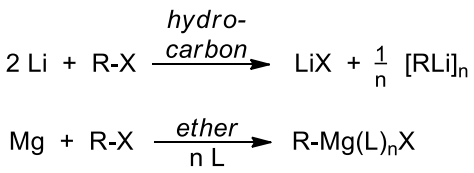
The direct synthesis of organocalcium compounds (heavy *Grignard* reagents) via the reduction of organyl halides with calcium powder succeeds straightforwardly for organic bromides and iodides that are bound at sp^2-hybridized carbon atoms. Extension of this strategy to alkyl halides is very limited and only the reduction of trialkylsilylmethyl bromides and iodides with activated calcium allows the isolation of corresponding heavy *Grignard* reagents. Substitution of only one hydrogen atom of the methylene moiety by a phenyl or methyl group directs this reduction toward the Wurtz-type coupling and the formation of calcium halide and the corresponding C-C coupling product. The fact that methylcalcium and benzylcalcium derivatives are stable in ethereal solvents suggests an unexpected reaction behavior of the intermediate organyl halide radical anions. Quantum chemical calculations verify a dependency between the ease of preparative access to organocalcium complexes and the C-I bond lengths of the organyl iodides. The bulkiness of the trialkylsilyl group is of minor importance. Chloromethyl-trimethylsilane does not react with activated calcium, however, halogen exchange reactions allow isolation of $[Me_3SiCH_2Ca(thf)_3(\mu\text{-}Cl)]_2$. Furthermore, the metathetical approach of $[Me_3SiCH_2Ca(thf)_4I]$ with $KN(SiMe_3)_2$ and the addition of pmdeta allow the isolation of heteroleptic $[Me_3SiCH_2Ca(pmdeta)\{N(SiMe_3)_2\}]$. In the reaction of this derivative with phenylsilane, the trimethylsilylmethyl group proves to be more reactive than the bis(trimethylsilyl)amido substituent.

Keywords: *Grignard* reaction, alkylcalcium reagents, calcium, direct synthesis, reduction reactions

Introduction

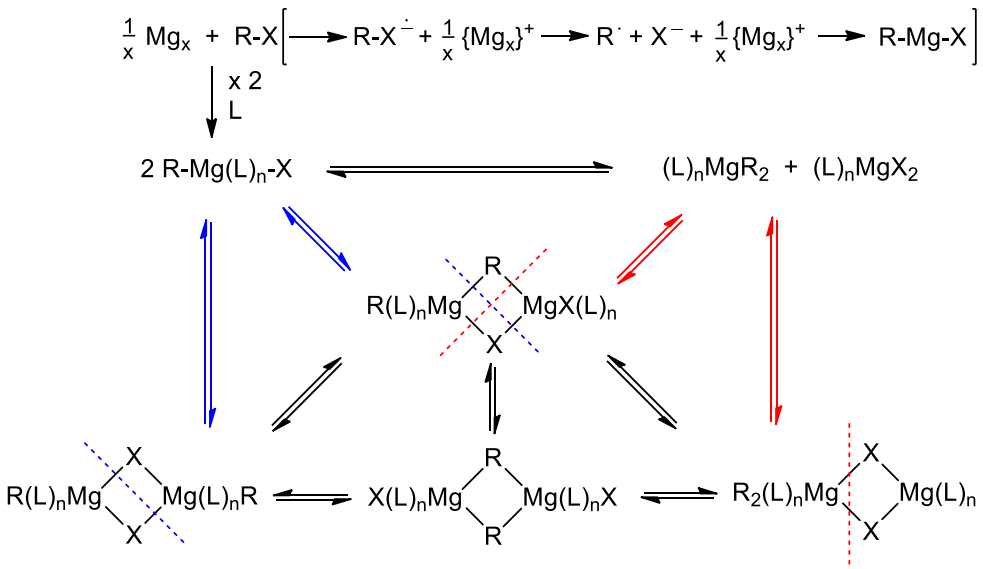
The direct syntheses of organolithium[1] and organomagnesium compounds[2] (*Grignard* reagents, Scheme 1) have been well-known for more than a century and represent common text book knowledge. The preparative procedures are straightforward, yields are commonly satisfactory and often isolation and structure determination of these highly air- and moisture-sensitive

organometallics is feasible.[3] Therefore, every chemistry student is familiar with umpolung reactions, i.e. the reaction of an organyl halide with an electropositive metal like lithium or magnesium.



***Scheme 1**: Preparation of organolithium and organomagnesium compounds (Grignard reagents) via direct synthesis (X = Cl, Br, I).*

In Scheme 2 a simplified electron transfer cascade as mode for the formation of *Grignard* compounds is given consisting of two single electron transfer (SET) steps from magnesium onto the organyl halide R-X. In the bottom part of this scheme the redistribution behavior in solution (aggregation and *Schlenk* equilibrium) is depicted.



***Scheme 2**: The Grignard reaction of magnesium with organyl halides R-X. The top row shows a simplified picture of the electron transfer steps. The bottom part of the scheme offers a brief overview on dinuclear species involved in the ligand scrambling reactions (Schlenk equilibrium).*

In Table 1, selected physical data of the convenient metals lithium, magnesium, calcium, and strontium are compared.[4] Calcium has a very similar electronegativity value as lithium leading to comparable ionicity of Li-C and Ca-C bonds. The standard potentials of lithium and calcium are quite similar whereas magnesium differs significantly with respect to these values. In this row, the largest atomization enthalpy is found for calcium leading to the highest melting and boiling points among these electropositive metals. The hydration enthalpies strongly depend on charge and size of ions with increasing charge and decreasing radius leading to larger absolute values.

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Table 1: Comparison of selected physical data of the s-block metals lithium, magnesium, calcium, and strontium.[4]

	Lithium	Magnesium	Calcium	Strontium
Electronegativity[a]	0.97	1.23	1.04	0.89
1st ionization potential (eV)	5.320	7.642	6.111	5.695
2nd 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}) [b]	-521	-1922	-1577	-1415
Radius of metal ion (pm) [b,c]	90	86	114	132
Standard potential E_0 (V, *vs* NHE) [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.

However, the transfer of the *Grignard* reaction to heavier alkaline earth metals has inherent challenges and diverse reasons account for the lack of an early straightforward development of organocalcium compounds of the type R-Ca-X.[5] On the one hand, these organometallics are very sensitive toward moisture (hydrolysis) and air (oxidation) due to very polar Ca-C bonds based on the electronegativity difference of calcium and carbon. On the other hand, the reduction of organic halides with calcium is accompanied by side reactions such as ether degradation (formation of RH), *Wurtz*-type coupling (R-R formation: R = alkyl, *Wurtz* reaction; R = alkyl, R' = aryl, *Wurtz-Fittig* reaction; R = aryl, *Fittig* reaction) or reduction of π-systems of aromatic systems (Birch-type reduction),[6] often leading to irreproducible results of the direct synthesis with calcium. In contrast, the reactivity of calcium metal itself (with aggravating influence of containing trace elements) is rather low and unlike lithium (which must be handled in an argon atmosphere because it reacts with nitrogen and oxygen yielding lithium nitride and oxide) and magnesium, activation (and occasionally purification) is required prior to its use in *Grignard*-type reduction reactions. Nevertheless, pyrophoric calcium powder still shows a limited reactivity because organyl chlorides are not suitable as substrates for the direct synthesis. From these studies it seems clear that the synthetic difficulties are of kinetic rather than thermodynamic origin since the heavy *Grignard* reagents benzylcalcium,[7] methylcalcium[8] and *n*-alkylcalcium derivatives[9] are known and can safely be handled in ethereal solvents. These challenges related to the direct synthesis initiated the development of alternative procedures (Scheme 3) with the salt metathesis reaction of organic alkali metal complexes with soluble calcium iodide being the favored method.[5,10]

(i) $2\ Ca + 2\ R\text{-}X \longrightarrow 2\ R\text{-}Ca\text{-}X \rightleftharpoons CaX_2 + CaR_2$

(ii) $Ca + 2\ HR \longrightarrow CaR_2 + H_2$

(iii) $CaL_2 + 2\ HR \longrightarrow CaR_2 + 2\ HL$

(iv) $2\ AR + CaX_2 \longrightarrow CaR_2 + 2\ AX$

(v) $Ca + MR_2 \longrightarrow CaR_2 + M \xrightarrow{+\ 2\ MR_2} Ca[MR_3]_2$

(vi) $LCaH + H_2C{=}CHR \longrightarrow LCa\text{-}CH_2\text{-}CH_2\text{-}R$

***Scheme 3**: Overview of synthetic procedures of organylcalcium complexes (L = anionic ligand like amido, ß-diketiminato groups and others), including (i) direct synthesis (Grignard reaction) with subsequent Schlenk equilibrium, (ii) direct metalation, (iii) organometallic metalation, (iv) metathetical approach (A = alkali metal, in most cases potassium; X = halide or pseudohalide), (v) transmetalation commonly yielding heterobimetallic complexes (M = Cu, Zn and others), and (vi) hydrometallation.*

In the early 1990s, the synthesis via co-condensation of organic substrate and calcium vapor as well as determination of the molecular structure of $[(dx)_2Ca\{CH(SiMe_3)_2\}_2]$ (dx = 1,4-dioxane) by the Lappert group[11] led to a vivid revival of the organocalcium chemistry. Approximately 15 years after this tremendous success, we developed a reliable synthesis of arylcalcium reagents via the atom-economic direct synthesis of the organic bromides or iodides with activated calcium in common organic solvents and determined molecular structures of arylcalcium complexes.[12] Convenient preparative procedures were developed for an ubiquitous use of this class of heavy *Grignard* reagents.[5] Alternative procedures are subject to limitations. Metalation reactions require very H-acidic substrates (like cyclopentadiene). Transmetalation protocols generally yield metalates.

Here we study the direct synthesis and the outcome of the direct synthesis with various alkyl halides. Furthermore, we propose an explanation for the observed challenges related to the direct synthesis of alkylcalcium halides as well as dialkylcalcium derivatives as a consequence of the *Schlenk*-type equilibrium.

Results and discussion

Limitations of the Direct Syntheses of Heavy Grignard Reagents

The reduction of organic halides with activated calcium commonly proceeds quite smoothly if the halide is bound to an sp^2-hybridized carbon atom, allowing the transfer of this procedure to alkenyl halides.[13] Alkylcalcium derivatives prepared by reduction of alkyl bromide or iodide with activated calcium are limited to very few representatives. As outlined above, the isolation of organocalcium derivatives with diverse alkyl groups such as benzyl,[7] methyl[8] or *n*-alkyl[9] by other preparative methods and elucidation of their molecular structures demonstrate that these organometallics are stable in ethereal media and hydrocarbons, suggesting that side reactions during the procedure itself are responsible for the failure of the direct synthesis of hydrocarbylcalcium halides.

Assuming a similar mechanism for the direct synthesis of heavy *Grignard* reagents as had been elucidated for the classic *Grignard* reactions,[14] the first reaction step would be a single electron transfer (SET) from calcium onto the organyl halide on the metal surface leading to a radical anion, which could be desorbed into the solution (Scheme 4). This radical anion could either dissociate into an alkyl radical and a halide anion or accept another electron leading to an alkyl anion and a halide anion. The anions would be captured at the positively charged metal surface whereas the electroneutral alkyl radicals could dissociate into the reaction solution where this radical had a limited lifetime depending on the reaction rates of recombination (R-R, *Wurtz*-type coupling product), solvent attack (R-H formation), and reduction (formation of the R^- carbanion). Now several reaction pathways would be feasible. The cation $[CaX]^+$ could be solvated and split off the metal particle. At the same time the alkyl radical could be reduced on the metal surface and then recombine to the heavy *Grignard* reagent R-Ca-X. Reversal of this latter reaction sequence would lead to reduction of the alkyl radical which then would bind to the metal, also yielding R-Ca-X which would then be solvated by Lewis bases and liberated into the reaction solution.

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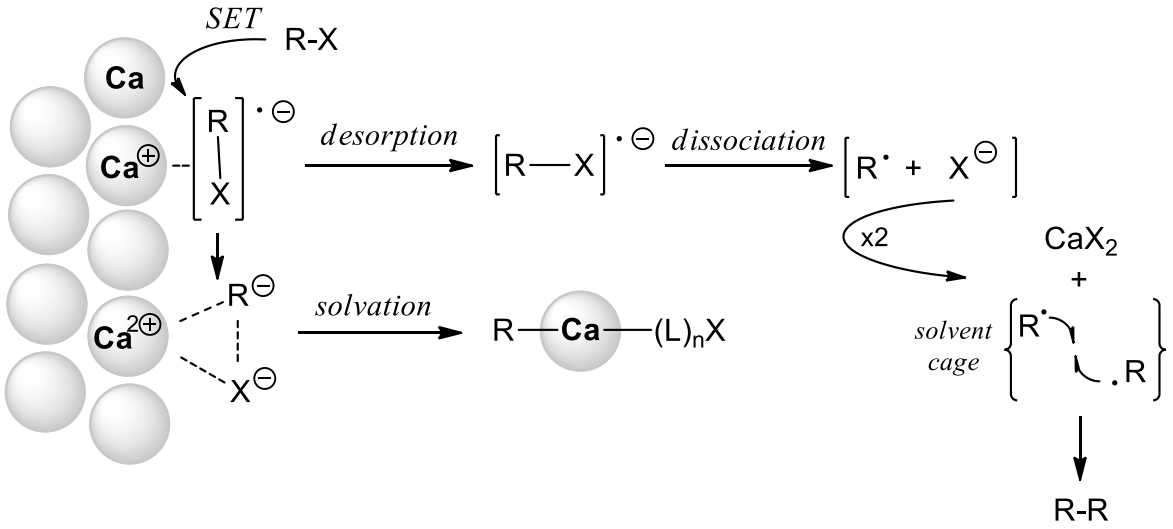


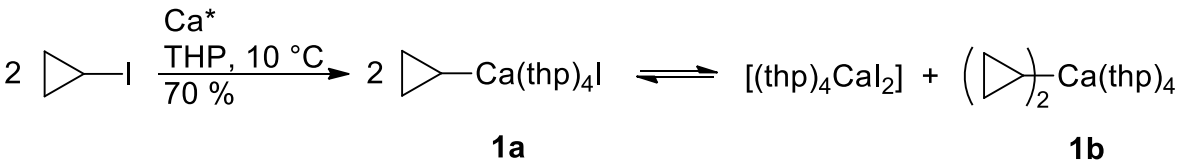
***Scheme 4**: The reaction of calcium metal with organyl halides R-X including the different consecutive steps forming the product of homo coupling (Wurtz-type reaction) and heavy Grignard reagent (organocalcium halide).*

In contrast to this, the general reaction of an organo halide with calcium meal leads to the isolation of the *Wurtz*-type coupling products; this could be traced directly to the properties of the metal. A key reaction step is desorption of a metal-ion out of the metal particle. This process is related to the atomization enthalpy, which is significantly larger for calcium than for magnesium (see Table 1). In the following, the metal ion is coordinated by solvent molecules. Solvation of magnesium and calcium ions by water (hydration, see Table 1)[6] and tetrahydrofuran molecules[15] shows that a larger radius expectedly and significantly reduces the absolute value of the solvation enthalpy. In conclusion, the desorption process of calcium ions is thermodynamically less favored than for magnesium ions. In addition, another SET step from the metal particle to the alkyl radical has to be considered. According to the ionization enthalpy, this should be more favorable in the case of calcium. However, this process can be related to the distance between the reaction partners (metal particle and alkyl radical) with the consequence of a slower SET for calcium. In conclusion, the overall process of the formation of a heavier *Grignard* reagent seems to be slower for calcium than for magnesium with the consequence that side reactions like radical dimerization or radical rearrangements gain significance.

Different reactivity patterns of magnesium and calcium have been observed in the aryl alkaline earth metal chemistry, too. 2,4,6-Tri(tert-butyl)phenyl halides[5] and 2,4,6-triphenylphenyl halides[16] react smoothly with magnesium whereas surprisingly different reaction patterns are observed if calcium is used for the reduction of these bulky aryl halides. If the reduction of 2,4,6-tri(tert-butyl)phenyl halide is performed with calcium, tunneling processes convert the intermediately formed tri(tert-butyl)phenyl radical into the 1-[3,5-di(tert-butyl)phenyl]-1,1-dimethylethyl radical.[17] Furthermore, lithium and magnesium are able to form dimetalated benzene with 1,4-diiodobenzene whereas the reaction of 1,4-$I_2C_6H_4$ with activated calcium selectively yields 4-iodophenylcalcium iodide.[18] The π-systems of oligocyclic aromatic halides tend to be reduced by calcium (leading to *Birch*-type reductions) much more easily than by magnesium.[6]

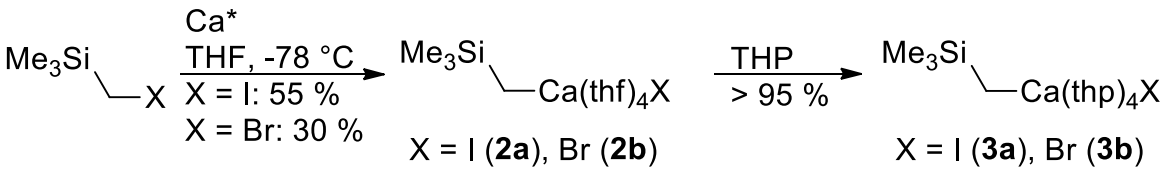
Therefore, we focused our studies on substitution patterns of the organyl halides that would enhance the life time of possible radical intermediates. Based on this approach, we started our

investigation with the reduction of cyclopropyl iodide with activated calcium because it is generally accepted that the carbon atoms of this alkyl group can be regarded as sp^2-hybridized.[19] Cyclopropylmagnesium derivatives[20] are known and cyclopropyl groups can be involved in stabilizing CC agostic interactions.[21] The reaction proceeded smoothly in tetrahydropyran (THP) at 10 °C according to Scheme 5 and yields of approximately 70 % could be achieved. This cyclopropylcalcium halide complex (**1a**) is highly soluble in ethereal solvents and a *Schlenk*-type equilibrium converts cyclopropylcalcium iodide **1a** into di(cyclopropyl)calcium **1b** and calcium diiodide. Crystallization efforts led to precipitation of well-known $[(thp)_4CaI_2]$[22] shifting the equilibrium toward the homoleptic complexes. Despite considerable efforts, growing of single crystals of cyclopropylcalcium derivatives suitable for X-ray diffraction experiments failed. Relevant ^{1}H NMR data includes a shielded H_α resonance at δ −1.65 (br m) and two sets of resonances for the diastereotopic H_β in the δ 0.20-0.40 (br m, 2H) and 0.50-0.75 (br m, 2H) ranges. In the $^{13}C\{^1H\}$ NMR spectrum, Ca-C_α resonates at δ 7.9 and the C_β atoms are observed at δ 7.0.



***Scheme 5**: Synthesis of tetrakis(tetrahydropyran)calcium cyclopropanide iodide in tetrahydropyran, also yielding thp complex of di(cyclopropyl)calcium via a Schlenk-type equilibrium.*

The reduction of trimethylsilylmethyl bromide and iodide with activated calcium in tetrahydrofuran yielded the corresponding alkylcalcium iodide (**2a**)[23,24] and bromide (**2b**) whereas Me_3SiCH_2Cl did not react with calcium powder. In order to enhance the durability in ethereal solvents, the thf ligands were exchanged by tetrahydropyran molecules (Scheme 6). The molecular structure and numbering scheme of $[Me_3SiCH_2Ca(thp)_4Br]$ (**3b**) is depicted in Figure 1. The structure is very similar to the homologous iodide congener $[Me_3SiCH_2Ca(thp)_4I]$ (**3a**).[23] The Ca1-C1 bond length exhibits a characteristic value of 250.0(4) pm. Steric requirements (i.e. repulsion between thp ligands and the bulky trimethylsilyl group) lead to a large Ca1-C1-Si1 bond angle of 143.9(2)°.



***Scheme 6**: Synthesis of trimethylsilylmethylcalcium bromide (X = Br, **2b**) and iodide (X = I, **2a**) as thf adducts and subsequent exchange of the ligated ether by tetrahydropyran yielding $[Me_3SiCH_2Ca(thp)X]$ with X = Br (**3b**) and I(**3a**).*

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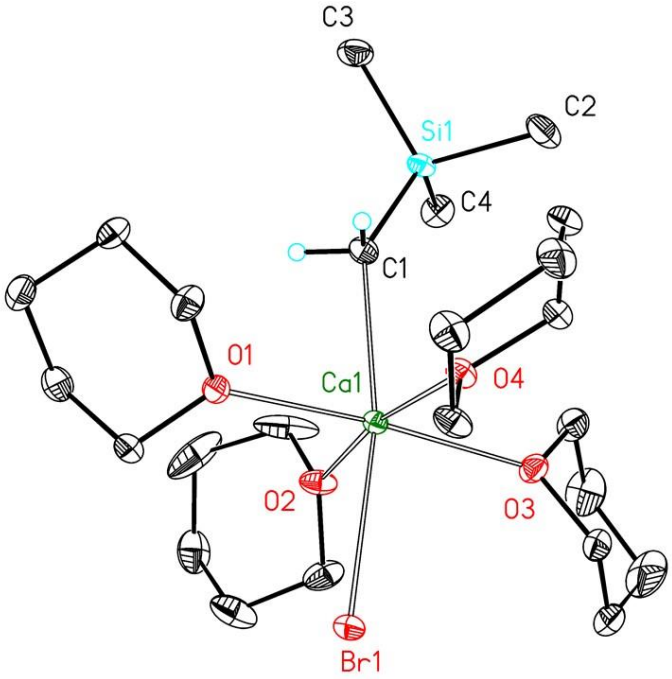
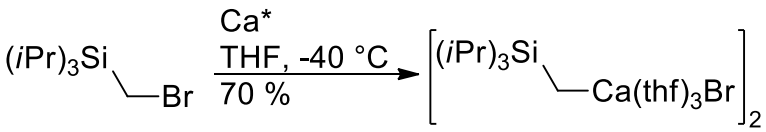


***Figure 1**: Molecular structure and atom labeling scheme of [$Me_3SiCH_2Ca(thp)_4Br$] (**3b**). The ellipsoids represent a probability of 30 %, only the H atoms at C1 are shown with arbitrary radii. Selected bond lengths (pm): Ca1-Br1 289.83(7), Ca-C1 250.0(4), Ca1-O1 239.5(2), Ca1-O2 241.3(3), Ca1-O3 239.3(2), Ca1-O4 236.9(2), Si1-C1 181.9(4), Si1-C2 188.8(4), Si1-C3 189.2(4), Si1-C4 188.4(4); bond angles (deg.): Br1-Ca1-C1 168.65(9), Ca1-C1-Si1 143.9(2), C1-Si1-C2 110.4(2), C1-Si1-C3 114.8(2), C1-Si1-C4 113.1(2), C2-Si1-C3 106.9(2), C2-Si1-C4 106.9(2), C3-Si1-C4 104.2(2).*

Thereafter, we studied bulkier alkyl halides and the reduction of bromomethyl-triisopropylsilane with activated calcium in THF at -40 °C. Again, high yields of 70 % were obtained. Recrystallization from a mixture of THF and pentane yielded single crystals of [iPr$_3$SiCH$_2$Ca(thf)$_3$(μ-Br)]$_2$ (**4**) with bridging bromide ions according to Scheme 7. The molecular structure and atom labeling scheme of complex **4** are depicted in Figure 2. The calcium atoms are in distorted octahedral coordination spheres with Ca1-C1 and Ca2-C11 bond lengths of 251.2(3) and 250.5(3) pm. The bromide bridges are slightly asymmetric with the larger Ca-Br distances *trans* to the alkyl substituent.



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***Scheme 7**: Synthesis of [(iPr)$_3$SiCH$_2$Ca(thf)$_3$Br]$_2$ (**4**) via reduction of bromomethyl triisopropylsilane with activated calcium in THF.*

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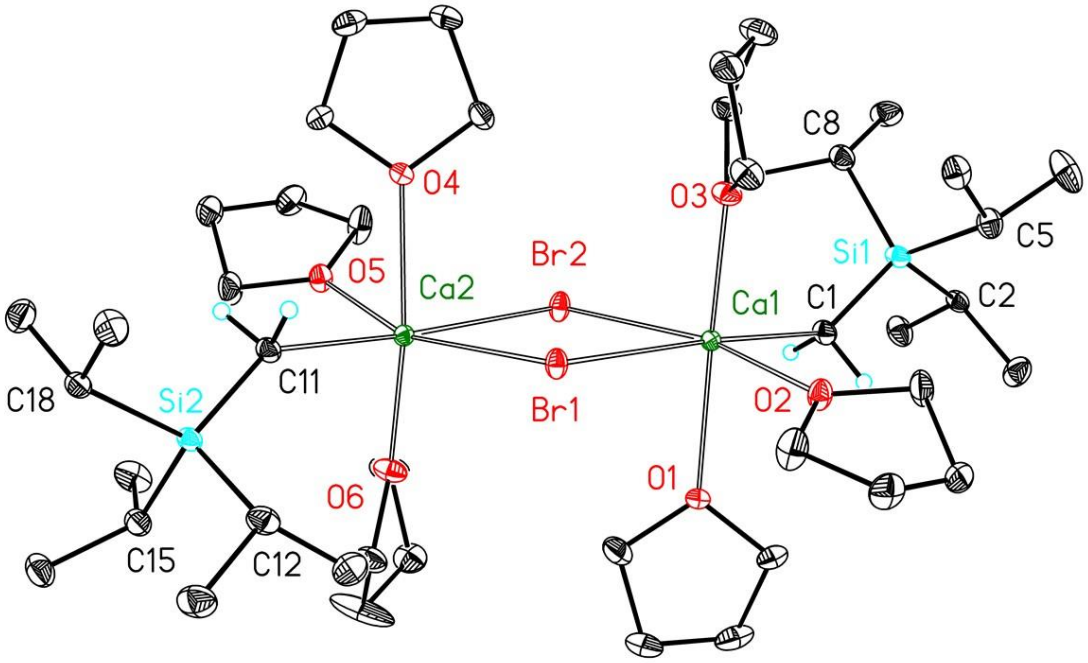

***Figure 2**: Molecular structure and atom labeling scheme of [iPr₃SiCH₂Ca(thf)₃(μ-Br)]₂ (**4**). The ellipsoids represent a probability of 30 %, only the H atoms of the methylene groups at C1 and C11 are shown with arbitrary radii. Selected bond lengths (pm): Ca1-Br1 303.35(7), Ca1-Br2 289.69(7), Ca2-Br1 290.09(7), Ca2-Br2 303.91(7), Ca1-C1 251.2(3), Ca1-O1 240.3(2), Ca1-O2 242.0(2), Ca1-O3 237.5(2), Ca2-C11 250.5(3), Ca2-O4 240.0(2), Ca2-O5 244.7(2), Ca2-O6 238.1(2), Si1-C1 182.9(3), Si1-C2 191.3(3), Si1-C5 193.6(4), Si1-C8 190.8(4), Si2-C11 183.7(3), Si2-C12 193.4(4), Si2-C15 190.6(4), Si2-C18 192.1(3); bond angles (deg.): Br1-Ca1-Br2 79.95(2), Ca1-Br1-Ca2 100.10(2), Br1-Ca2-Br2 79.79(2), Ca1-Br2-Ca2 100.06(2), C1-Ca1-Br1 176.07(8), C1-Ca1-Br2 98.82(9), C11-Ca2-Br1 97.62(8), C11-Ca2-Br2 175.11(8), Ca1-C1-Si1 140.0(2), Ca2-C11-Si2 142.8(2).*

Substitution of the silicon atom in Me_3SiCH_2X by a carbon and use of neopentyl halide led to negligible alkalinity of the reaction mixture and we were unable to isolate neopentylcalcium complexes from such a procedure but large amounts of the *Wurtz*-type coupling product 2,2,5,5-tetramethylhexane were obtained. Furthermore, substitution of trimethylsilylmethyl halide with a methyl or tert-butyl group at the methylene moiety yielding 1-trimethylsilyl-1-iodoethane and 1-trimethylsilyl-1-iodo-2,2-dimethylpropane led to the formation of the *Wurtz*-type coupling products and significant concentrations of *Grignard*-type alkylcalcium complexes were not observed. In Table 2, consumption of the substrates and yields of organylcalcium derivatives from the direct synthesis of activated calcium with organyl halides are summarized. Chloroalkanes and -arenes cannot be reduced with activated calcium and no reaction is observed. This observation confirms that calcium is significantly less reactive than magnesium in direct synthesis of *Grignard*-type reagents. This finding is in agreement with the formation of a bis(*Grignard*) reagent from 1,4-diiodobenzene whereas calcium only allows the isolation of 4-iodophenylcalcium iodide.

Table 2: Conversion of selected organyl halides into the corresponding organylcalcium reagents via a direct synthesis of the organyl halide with activated calcium in tetrahydrofuran.

Substrate	Organylcalcium halide	Consump. (%) [a]	Convers. (%) [b]	Yield (%) [c]	Ref.
Ph-Cl	[Ph-Ca(thf)$_4$Cl]	0	0	0	[12]
Ph-Br	[Ph-Ca(thf)$_4$Br]		71		[12,25]
Ph-I	[Ph-Ca(thf)$_4$I]		93	70	[12,25]

4-I-C_6H_4-I	[4-I-C_6H_4-Ca(thf)$_4$I]	> 95	95	20	[12]
Mes-Br	[Mes-Ca(thf)$_4$Br]		< 5	0	[12]
Mes-I	[Mes-Ca(thf)$_4$I]		86	19	[26]
2,4,6-(*t*Bu)$_3C_6H_2$-Br	[2,4,6-(*t*Bu)$_3C_6H_2$-Ca(thf)$_4$Br]	> 90	0	0	[5]
2,4,6-$Ph_3C_6H_2$-Br	[2,4,6-$Ph_3C_6H_2$-Ca(thf)$_4$Br]	> 90	> 80 [d]	0	[16]
Me-I	[Ca(thf)$_3$I(μ-Me)]$_2$	> 90	0	0	
Me_3SiCH_2-Cl	[Me_3SiCH_2-Ca(thf)$_4$Cl]	0	0	0	
Me_3SiCH_2-Br	[Me_3SiCH_2-Ca(thf)$_4$Br]		30	13	
Me_3SiCH_2-I	[Me_3SiCH_2-Ca(thf)$_4$I]		70	55	[23,27]
Me_3CCH_2-I	[Me_3CCH_2-Ca(thf)$_4$I]	> 90	< 5	0	
Me_3SiCH(Me)-I	[Me_3SiCH(Me)-Ca(thf)$_4$I]	> 90	< 5	0	
Me_3SiCH(*t*Bu)-I	[Me_3SiCH(*t*Bu)-Ca(thf)$_4$I]	> 90	< 5	0	
iPr_3SiCH_2-Br	[*i*Pr_3SiCH_2-Ca(thf)$_3$Br]$_2$	> 80	70	12	

[a]) Consumption refers to the substrate. [b]) Conversion to an organocalcium complex was estimated by an acid-base titration of an aliquot of the reaction solution; differentiation of organylcalcium halide and diorganylcalcium is not possible by this method. [c]) Yield refers to isolated crystalline compound. [d]) The reduction of 2,4,6-triphenylphenyl halide with calcium in THF intermediately yields the heavy *Grignard* reagent which converts into the inverse sandwich complex [{(thf)$_3$Ca}$_2$(μ-1,3,5-$Ph_3C_6H_3$)] with calcium(I) ions (see text).

Quantum Chemical Investigations

To shed light on the strikingly different behavior of the studied alkyl halides, DFT calculations were performed. The fact that the instability of alkylcalcium halides (or dialkylcalcium complexes) is not responsible for the failure of the direct synthesis of alkylcalcium halides suggests that intermediates behave differently in these reactions. In the case of the *Grignard* formation, it is well accepted that the initial reaction step is a single electron transfer from the magnesium particle onto the alkyl halide molecule, leading to a radical anion (see Scheme 1; for a well-balanced discussion of the *Grignard* reaction see the excellent review of Garst and Soriaga[14]). It has been concluded that the key step is the reduction of the alkyl halide and that the first electron transfer (leading to the radical anion) is the most difficult step depending on the substrates electrophilicity.[28] Therefore, we studied these species with the help of quantum chemical investigations. We chose the density functional theory with the functional B97D3 and the basis set 6-311++G** as level of theory. The relaxed geometry of the mono reduced radical anion of R-X was calculated and for comparison, we also included iodobenzene in these studies. The computed bond lengths of the species lie in the range between 300 and 380 pm (see Table 3); in electroneutral organic iodides the C-I bond lengths vary between 199 and 214 pm depending on the hybridization of the carbon atom.[29]

Table 3: Calculated bond lengths (B97D3/6-311++G**) of several iodoalkanes and -arenes radical anions.

Organohalide R-I	Bond length of $[R\text{-}I]^{-\cdot}$
Ph-I	302.5
*c*Pr-I	329.8
$PhCH_2$-I	343.1
PhC(*t*Bu)H-I	375,1
PhC($SiMe_3$)H-I	351.0
Me_3SiCH_2-I	342.3
Me_3SiCH(Me)-I	362.9
Me_3SiCH(*t*Bu)-I	359.7
(*i*$Pr)_3SiCH_2$I	340.1
Me-I	353.7

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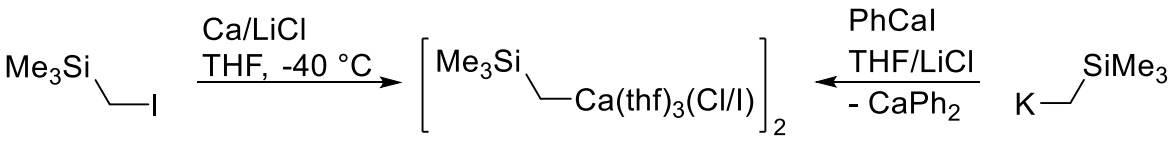
Me_3CCH_2-I	366.7

The C-I bonds show a significant elongation upon reduction and formation of the radical anion. Scheme 8 provides a plot of the C-I bond length as a function of the ease of formation of Grignard reagent or *Wurtz* product. It is seen that the longer the C-I bond in the radical anion, the easier the formation of the Wurtz coupling product. Slight elongation of the C-I bonds after the SET step (C-I bond lengths below 330 pm) requires that the iodine atom is bound to an sp^2 hybridized carbon atom. These iodohydrocarbons allow the isolation of organocalcium derivatives in high yields with iodobenzene as the ideal candidate. Therefore it is not surprising that many arylcalcium complexes have been described in recent years. In the intermediate region (C-I bond lengths between 330 and 343 pm; depicted in orange in Scheme 8), iodoalkanes with trialkylsilyl substituents are located. They can be reduced to the corresponding alkylcalcium complexes; however, the yields are lower due to side reactions such as *Wurtz*-type coupling. If the C-I bond lengths of the radical anions lie above 343 pm, the *Wurtz*-type coupling is the dominant reaction and the C-C coupling product is obtained nearly quantitatively.

Scheme 8*: Plot of the iodoalkane and -arene radical anions calculated C-I bond lengths (see Table 3). The green background symbolizes the region with straightforward Grignard-type reactions of the organic iodide with calcium. The orange color contains radical anions which lead to formation of the Grignard-type reagent and Wurtz coupling products. The red region shows iodoalkanes which are reduced solely to the Wurtz coupling products.*

Halide Exchange Reactions

The reduction of chloromethyltrimethylsilane with calcium powder failed. Therefore, a halogen exchange was realized to study the influence of a lighter halogen on the NMR data and on structural parameters. Thus, the reduction of iodomethyltrimethylsilane with calcium was performed in THF in the presence of lithium chloride, yielding a mixture of trimethylsilylmethylcalcium halides. However, a quantitative halide exchange was not achieved by this simple procedure. The attempt to prepare an alkyl-arylcalcium complex via the reaction of phenylcalcium iodide with KCH2SiMe3 in tetrahydrofuran, also containing LiCl, led to quantitative formation of $[(thf)_4CaPh_2]$ and a few single crystals of dinuclear $[Me_3SiCH_2Ca(thf)_3(\mu\text{-}Cl)]_2$ (**2c**) suitable for X-ray diffraction experiments (Scheme 9). The molecular structure and atom numbering scheme of $[Me_3SiCH_2Ca(thf)_3(\mu\text{-}Cl)]_2$ (**2c**) are depicted in Figure 3.



2c

***Scheme 9**: Synthesis of trimethylsilylmethylcalcium chloride via direct synthesis in LiCl-containing THF solutions or via a metathetical approach of phenylcalcium iodide with trimethylsilylmethyl potassium in THF in the presence of LiCl.*

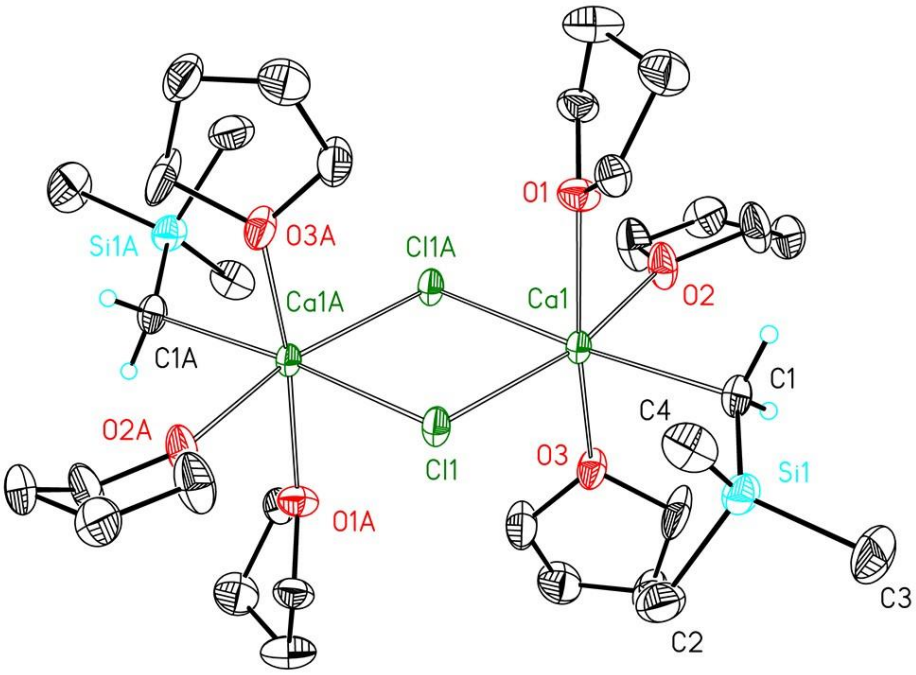


***Figure 3**: Molecular structure and atom labeling scheme of $[Me_3SiCH_2Ca(thf)_3(\mu\text{-}Cl)]_2$ (**2c**). The ellipsoids represent a probability of 30 %, only the H atoms at C1 are drawn with arbitrary radii. Symmetry-related atoms (-x+2, -y+1, -z+1) are marked with the letter "A". Selected bond lengths (pm): Ca1-Cl1 273.6(1), Ca1-Cl1A 278.9(1), Ca1-C1 252.4(4), Ca1-O1 239.7(3), Ca1-O2 242.5(3), Ca1-O3 238.9(3), Si1-C1 181.2(4), Si1-C2 189.4(5), Si1-C3 189.9(5), Si1-C4 187.3(5); bond angles (deg.): Cl1-Ca1-Cl1A 82.36(3), Ca1-Cl1-Ca1A 97.64(3), Cl1-Ca1-C1 104.6(1), Cl1A-Ca1-C1 173.0(1), Ca1-C1-Si1 119.0(2).*

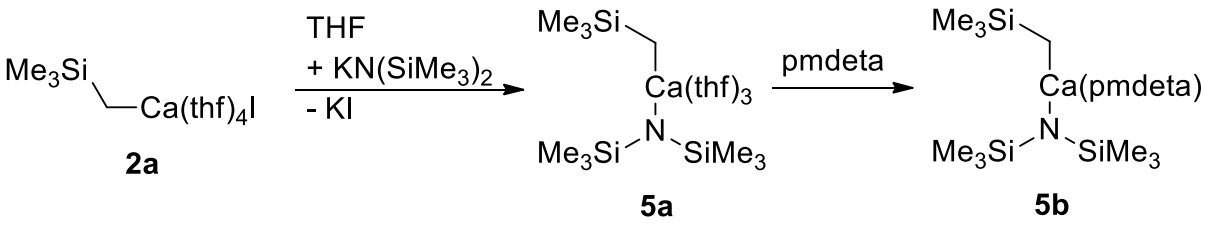
Selected structural parameters are listed in Table 4 together with those of related compounds. In all these complexes, the calcium atoms are in distorted octahedral environments. Aggregation to dinuclear complexes of the type $[R_3SiCH_2Ca(thf)_3(\mu\text{-}X)]_2$ reduces steric strain because a bulky ether ligand is substituted by a bridging halide ion. This aggregation allows a Ca1-C1-Si1 bond angle of 119.0(2)° for **2c**. The very bulky triisopropylsilyl group enforces aggregation (i.e. substitution of a thf ligand by a bridging halide ion) and large Ca-C-Si angles are still inevitable but the preferred coordination number of six can be realized. The Ca-C bond lengths vary over a very narrow range regardless of aggregation and bulkiness of the trialkylsilyl group. A similar finding is valid for the Ca-O distances to the ligated ether molecules. Unique properties characterize the trialkylsilylmethyl groups. The Si-C_R bond lengths to the methyl and isopropyl groups are significantly larger than the Si-C_{Ca} distance to the calcium-bound carbon atom. This shortening is a consequence of negative hyperconjugation, the backdonation of electron density from the carbanion into σ*(Si-C_R) bonds of the trialkylsilyl groups as discussed earlier in detail.[23]

Table 4: Comparison of selected structural parameters (average values, bond lengths (pm) and angles (deg.)) of ether adducts of trialkylsilylmethylcalcium halides with hexa-coordinate calcium centers.

	$[R_3SiCH_2Ca(L)_3(\mu\text{-}Cl]_2$	$[R_3SiCH_2Ca(L)_4Br]$	$[R_3SiCH_2Ca(L)_4I]$	$[R_3SiCH_2Ca(L)_3(\mu\text{-}Br)]_2$
Compound	**2c**	**3b**	**3a**	**4**

R	Me	Me	Me	*i*Pr
L	thf	thp	thp	thf
Ca-C	252.4(4)	250.0(4)	252.7(3)	250.8
Ca-X	273.6(1), 278.9(1)	289.83(7)	319.11(3)	289.9, 303.6
Ca-O	240.4	239.3	239.9	240.4
Si-C_{Ca}	181.2(4)	181.9(4)	183.1(3)	183.3
Si-C_R	188.9	188.8	188.2	192.0
C_{Ca}-Ca-X	104.6(1), 173.0(1)	168.65(9)	170.53(7)	98.2, 175.6
Ca-C_{Ca}-Si	119.0(2)	143.9(2)	131.2(1)	141.4
Ref.	This work	This work	[28]	This work

The substitution of a halide in arylcalcium iodides via a metathetical approach with potassium pseudohalides (like e.g. bis(trimethylsilyl)amide, diphenylphosphanide) was already investigated.[30] Furthermore, the synthesis of bis(trimethylsilylmethyl)calcium followed a similar procedure via the reaction of trimethylsilylmethylcalcium halide with KCH_2SiMe_3.[27] A similar approach was studied for trimethylsilylmethylcalcium iodide to elucidate the influence of an alkyl group. Thus [Me_3SiCH_2-$Ca(thf)_4I$] was reacted with potassium bis(trimethylsilyl)amide in tetrahydrofuran yielding the corresponding heteroleptic complex [Me_3SiCH_2-$Ca(thf)_3\{N(SiMe_3)_2\}$] (**5a**) according to Scheme 10. Substitution of all thf ligands by tridentate *N,N,N′,N″,N‴*-pentamethyldiethylenetriamine (pmdeta) allowed crystallization of [Me_3SiCH_2-$Ca(pmdeta)\{N(SiMe_3)_2\}$] (**5b**) with penta-coordinate calcium centers.



***Scheme 10**: Metathetical approach for the synthesis of [Me_3SiCH_2-$Ca(thf)_3\{N(SiMe_3)_2\}$] (**5a**) and subsequent ligand exchange yielding [Me_3SiCH_2-$Ca(pmdeta)\{N(SiMe_3)_2\}$] (**5b**).*

Molecular structure and atom labeling scheme of [Me_3SiCH_2-$Ca(pmdeta)\{N(SiMe_3)_2\}$] (**5b**) are depicted in Figure 4. Despite a smaller coordination number of calcium the Ca1-C1 bond length remains unchanged and a typical value of 253.2(2) pm is observed. The Ca1-N1 distance of 232.5(2) pm is slightly elongated compared to [$(dme)Ca\{N(SiMe_3)_2\}_2$] (227.1(3) pm, dme = 1,2-dimethoxyethane)[41] and [$(thf)_2Ca\{N(SiMe_3)_2\}_2$] (229.4(3) and 230.9(3) pm)[42] with tetra-coordinate metal centers in distorted tetrahedral coordination spheres. The Ca-N_{amide} bond lengths in [$(tmeda)Ca\{N(SiMe_3)_2\}_2$] are elongated to 231.5(1) pm[43] verifying steric strain induced by the bulky tmeda ligand. Despite small N1-Si2/3 bond lengths only a slightly enlarged Si2-N1-Si3 bond angle of 124.5(1)° is observed in derivative **5**.

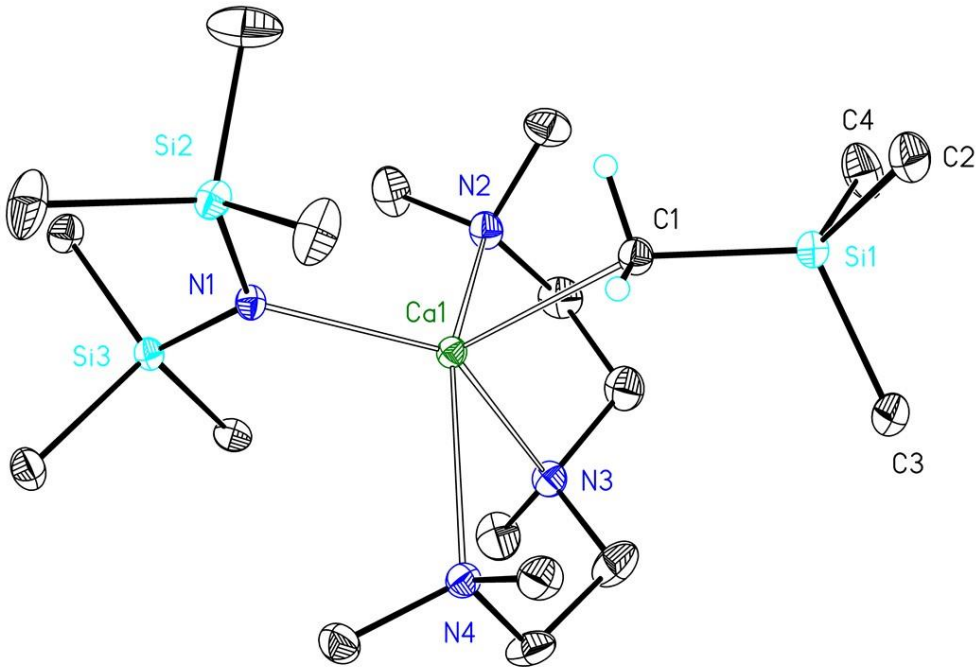
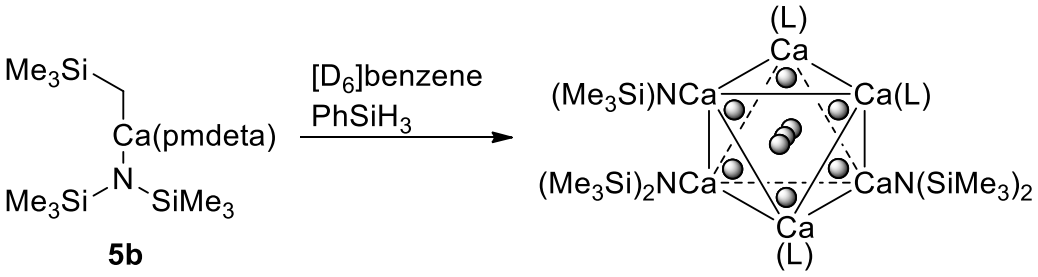


***Figure 4**: Molecular structure and atom labeling scheme of [Me_3SiCH_2-Ca(pmdeta){$N(SiMe_3)_2$}] (**5b**). The ellipsoids represent a probability of 30 %, only the hydrogen atoms at C1 are drawn with arbitrary radii. Selected bond lengths (pm): Ca1-N1 232.5(2), Ca1-C1 253.2(2), Ca1-N2 263.1(2), Ca1-N3 255.8(2), Ca1-N4 258.5(2), C1-Si1 182.7(2), Si1-C2189.1(3), Si1-C3 188.6(3), si1-C4 188.1(3), N1-Si2 169.2(2), N1-Si3 168.9(2), Si2-C5 187.2(2), Si2-C6 187.0(3), Si2-C7 189.0(3), Si3-C8 188.1(2), Si3-C9 188.7(2), Si3-C10 188.4(2); bond angles (deg.): N1-Ca1-C1 115.64(7), Ca1-C1-Si1 142.2(1), Ca1-N1-Si2 122.48(9), Ca1-N1-Si3 112.47(9), Si2-N1-Si3 124.5(1).*

Furthermore, the pmdeta adduct of trimethylsilylmethylcalcium bis(trimethylsilyl)amide **5b** was combined with phenylsilane in [D_6]benzene as depicted in Scheme 11 to elucidate whether the alkyl or the amido group is preferably transferred to the silicon atom. NMR studies revealed that the known hexanuclear hydrido amido complex [(pmdeta)Ca_6H_9{$N(SiMe_3)_2$}$_3$] was formed. The nature of this complex had already been authenticated by Harder and coworkers via NMR experiments and crystal structure determination.[34] Obviously, the transfer of the alkyl groups is favored whereas the bulky amido anions and the pmdeta ligands effectively shield the Ca_6H_9 calcium hydride cage (Scheme 11).



***Scheme 11**: Reaction of [Me_3SiCH_2-Ca(pmdeta){$N(SiMe_3)_2$}] (**5b**) with excess of phenylsilane yielding [(pmdeta)Ca_6H_9{$N(SiMe_3)_2$}$_3$]. The shaded balls represent the hydrogen ions of the Ca_6H_9 calcium hydride cage (L = pmdeta). The lines clarify the octahedral arrangement of the calcium atoms.*

Conclusion

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The discrepancy between the inertness of calcium metal and the enormous reactivity of its organocalcium compounds (heavy *Grignard* reagents) has so far hampered a vast development of the organic chemistry of this alkaline earth metal in contrast to the importance and broad application of classic *Grignard* reagents. On the one hand, a high atomization energy of the metal (20 % larger than for Mg) and low absolute solvation energies of the ions (22 % smaller than for Mg^{2+}) synergistically disfavor the *Grignard* reaction with calcium. Due to a larger radius of calcium (Ca: 197.4, Ca^{2+}: 114; Mg: 159.9, Mg^{2+}: 86 pm)[26] a closer approach of the organyl halide onto the surface of the alkaline earth metal particle for the SET reaction is possible for the lighter congener. These factors disfavor the formation of a heavy *Grignard* reagent of the type RCaX. On the other hand, the enormous reactivity of organylcalcium derivatives renders side reactions like ether degradation and *Wurtz*-type coupling reactions more detrimental.

However, the straightforward synthesis of arylcalcium halides and diarylcalcium established a promising heavy *Grignard* chemistry of calcium. Activation of calcium is required to overcome the inertness of the metal. The direct synthesis is an adequate strategy to reduce organyl halides with the halogen atom bound to a sp^2-hybridized carbon atom and reduction of alkenyl- and cyclopropyl bromides and iodides with calcium yields the corresponding organocalcium complexes. The reduction of alkyl halides is significantly more intricate and only the reaction of trialkylsilylmethyl bromide and iodide with calcium lead to the formation of alkylcalcium halides. The substitution of only a single hydrogen atom of the methylene fragment by a methyl group precludes the formation of the corresponding heavy *Grignard* reagent and only the *Wurtz*-type coupling product forms. The direct synthesis is also inapplicable for the synthesis of benzyl-, methyl- and neopentylcalcium compounds even though methylcalcium and benzylcalcium complexes areperfectly stable in ethereal solutions.

Quantum chemical calculations verify a very strong influence of the C-I bond lengths in organyl iodide radical anions varying between approximately 300 and 380 pm with iodobenzene showing the smallest C-I bond length and alkyl iodides having the largest values. Radical anions with C-I bond lengths below 330 pm smoothly form the heavy *Grignard* reagents R-Ca-I via a second SET step. For radical anions with intermediate C-I distances the formation of the heavy *Grignard* reagent competes with the *Wurtz*-type C-C coupling reaction whereas all radical anions with long C-I bonds yield the C-C coupling product besides calcium iodide. This finding can be interpreted in the sense that the second SET step is delayed and the organyl iodide radical anions with long (weak) C-I bonds dissociate yielding the organyl radicals (which recombine to R-R) and the iodide anions (which form CaI_2). Organyl iodide radical anions with short C-I bonds are significantly less prone to dissociation and a second SET step yields carbanions and iodide ions leading to the formation of the heavy *Grignard* reagent R-Ca-I.

The calcium ions prefer an octahedral coordination sphere. Enhancement of steric strain leads to substitution of an ether ligand by a bridging halide, maintaining the coordination number of six. This behavior is evident for the trimethylsilylmethylcalcium halides. The bromide and iodide ions show large distances to the calcium ions of 289.8 and 319.1 pm, respectively, whereas the short Ca-Cl bond increases steric repulsion within the complex. This steric pressure leads to dissociation of one ether ligand and dimerization via bridging halide ions. Enhancement of steric repulsion by replacement of the Me_3SiCH_2 group by the bulkier $i$$Pr_3SiCH_2$ substituent induces dissociation of one ether ligand as well.

The challenges related to the atom economic direct synthesis of heavy *Grignard* reagents are related to the retardation of the second SET reaction. One strategy for future investigations is doping of the calcium prior to use with other (electropositive) metals. Addition of electron transfer catalysts could also alleviate this hindrance.

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Experimental Section

Materials and methods: All manipulations were carried out in an inert nitrogen or argon atmosphere using standard *Schlenk* techniques, if not otherwise noted. Tetrahydrofuran, tetrahydropyran, and pentane were dried over KOH and subsequently distilled over sodium/benzophenone in a nitrogen atmosphere prior to use. PMDETA and all used alkyl halides were dried over CaH_2. Deuterated solvents were dried over sodium, distilled, degassed, and stored under nitrogen over sodium. ^{1}H, $^{13}C\{^{1}H\}$, and $^{29}Si\{^{1}H\}$ NMR spectra were recorded on Bruker Avance 400 and Fourier 300 spectrometers. Chemical shifts are reported in parts per million relative to $SiMe_4$ as an external standard referenced to the solvents residual proton signal (^{1}H and $^{13}C\{^{1}H\}$). Bromocyclopropane was purchased from Alfa Aesar. Benzyl bromide was purchased from Merck. Me_3CCH_2I and $KN(SiMe_3)_2$ were purchased from Sigma Aldrich. The starting materials $[(thp)_4Ca(CH_2SiMe_3)I]$,[30] PhCH(*t*Bu)Br,[35] $PhCH(SiMe_3)Br$,[36] *t*$BuCHI_2$,[37] *i*$Pr_3SiCHBr_2$,[38] Me_3SiCH_2Br,[39] and $Me_3SiCH(Me)I$[40] were synthesized according to literature protocols. KCH_2SiMe_3 was prepared by the metal-exchange reaction of $LiCH_2SiMe_3$ with KO*t*Bu in pentane. $LiCH_2SiMe_3$ was synthesized from Li ribbons and $ClCH_2SiMe_3$. Purity was controlled by NMR spectroscopic measurements, by determination of the alkalinity of an aliquot of the reaction solution and by complexometric titration of the Ca content with EDTA.

Synthesis of iodocyclopropane: In an argon filled glovebox, a Li ribbon (1.5 g, 0.22 mol) was cut into small pieces and placed in a *Schlenk* flask with 150 mL of diethyl ether. A solution of bromocyclopropane (10.0 g, 0.0826 mol) in 150 mL of Et_2O was added dropwise at 0 °C over a period of 3 hours. Then the slurry was stirred at r.t. overnight to afford a cloudy suspension also containing unreacted Li chunks. The suspension was filtered and the resulting solution was cooled down to –78 °C. A solution of I_2 (20 g, 0.079 mol) in Et_2O (150 mL) was added dropwise till the persistence of a brown colour. The solution was warmed to r.t. and treated with water and then with an aqueous Na_2SO_3 solution. The organic phase was separated and dried over anhydrous $MgSO_4$. Et_2O was removed by distillation at atmospheric pressure. Then CaH_2 was added and the slurry was stirred overnight. The brown residue was purified by trap-to-trap distillation to afford a colourless liquid (8.94 g, 64%) iodocyclopropane. The analytical data are in accordance with literature values.[41]

Synthesis of $Me_3SiCH(tBu)I$ (1-iodo-1-trimethylsilyl-2,2-dimethylpropane): A solution of 2.5M *n*BuLi (10.6 mL, 26.5 mmol) in hexane was added at -78 °C to a solution of $HN(iPr)_2$ (3.7 mL, 26.5 mmol) in 20 mL of a mixture of THF and Et_2O (1:1). The solution was stirred for 15 min and then cooled to –115 °C and then 17 g of *t*$BuCHI_2$ (13 mmol) were added, imminently leading to an orange-red suspension. After 15 minutes, 1.7 mL of Me_3SiCl were added at the same temperature. The slurry was stirred for additional 30 min and then warmed to r.t. The reaction mixture was quenched with water and Et_2O. The combined organic phase was washed with water and then dried with anhydrous Na_2SO_4. The solvent was removed in vacuum and CaH_2 was added to the residue. The product was obtained by trap to trap condensation, yielding 3.1 g of a colorless liquid (yield: 89 %, purity (GC): 95 %) containing small amounts of Me_3CCH_2I (5 %). ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ = 0.27 (s, 9H), 1.19 (s, 9H), 3.38 (s, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz): δ = 1.9, 30.9, 35.5, 44.4. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$, 79.5 MHz) δ = 4.0. IR: 2955 m, 2897 w, 2867 w, 1474 w, 1461 w, 1392 w, 1364 m, 1260 m, 1249 s, 1224 s, 1144 w, 1085 w, 1059 w, 1017 w, 935 w, 907 w, 836 s, 765 w, 751 w, 686 w, 617 w, 580 w. HR-MS (EI-MS): $[M\text{-}Me]^+$ $C_7H_{16}ISi^+$: calc.: 255.0060, found: 255.0044.

Synthesis of iPr_3SiCH_2Br: *i*$Pr_3SiCHBr_2$ (1.015 g, 3.07 mmol) was dissolved in 15 mL of THF and cooled to –115 °C. A 2.5M hexane solution of *n*BuLi (1.23 mL, 3.07 mmol) was slowly added to this solution. The yellow solution was stirred for 5 min and then quenched with 5 mL of MeOH at this temperature. After warming to r.t., water and Et_2O were added and the organic phase isolated and dried with

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anhydrous Na_2SO_4. The solvent was removed in vacuum and CaH_2 was added to the clear colorless liquid. The product was obtained by trap-to-trap condensation, yielding 750 mg of a colorless liquid of iPr_3SiCH_2Br (97 %). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.06 (d, 18H, J = 6.32 Hz), 1.15 (m, 3H, J = 6.32 Hz), 2.58 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ = 18.5, 12.2, 10.8. $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 79.5 MHz): δ = 4.81. IR: 2941 s, 2890 m, 2965 s, 1461 s, 1383 m, 1366 w, 1247 w, 1134 w, 1068 w, 1016 w, 1000w, 918 w, 881 s, 717 s, 663 m, 617 m 594 m, 570 m. HR-MS (EI-MS): $[M\text{-}i\text{Pr}]^+$ $C_7H_{16}BrSi^+$: calc.: 207.0199, found: 207.0197.

General procedure for the reaction of activated calcium with alkyl halide: Activated calcium (20 mg, 0.5 mmol, 1.1 equiv.) was suspended in 3 mL of THF and cooled to –78 °C prior to addition of alkyl halide (0.45 mmol, 1 equiv.). The reaction mixture was stirred for 1h at –78 °C and then slowly warmed to r.t. Then all solids were removed by filtration. This solution was analysed by acidimetric titration. For this purpose 1 mL was hydrolyzed, 3 mL of Et_2O were added and the phases were separated. The organic layer was dried with anhydrous Na_2SO_4 and directly analysed by GC/MS.

*Synthesis of cyclopropylcalcium iodide (**1a**):* Iodocyclopropane (1.53 g, 9.13 mmol) was added at 10 °C to a suspension of Ca* (366 mg, 9.13 mmol) in 20 mL of tetrahydropyran. The slurry was shaken for two hours. Then the reaction mixture was warmed to r.t. and unreacted calcium was removed by filtration. Acidimetric titration of an aliquot of the resulting red solution gave a conversion of 70 %. Repeated concentration of the solution by evaporation under vacuum and cooling to –40 °C afforded several crops of colorless crystals of $[(thp)_4CaI_2]$. Once no more precipitate was obtained, the mother liquor was evaporated to dryness and washed several times with pentane. The brown solid residue consisted of a mixture of cyclopropyl calcium iodide and dicyclopropyl calcium (400 mg). Due to the composition as a mixture, reliable elemental analysis were not obtained. ^{1}H NMR ($[D_8]$THF, 400.13 MHz): δ = -1.65 (bm, 1H, Hα), 0.20-0.40 (br m, 2H, Hβ/β'), 0.50-0.75 (br m, 2H, Hβ/β'), 1.49 (m, thp), 1.60 (m, thp), 3.53 (t, J = 5.14 Hz, thp). $^{13}C\{^1H\}$ NMR ($[D_8]$THF, 125.8 MHz): δ = 6.98 (C_β), 7.89 (C_α), 24.6 (thp), 27.6 (thp), 69.1 (thp).

*Synthesis of $[(thp)_4CaBr(CH_2SiMe_3)]$ (**3b**)*: Activated calcium (482 mg, 12.02 mmol, 1.1 equiv.) was suspended in 20 mL of THF. The suspension was cooled to –78 °C before 1.9 g of $BrCH_2SiMe_3$ (10.9 mmol, 1 equiv.) were added. The reaction mixture was shaken for 2h at –78 °C. Then all solids were removed by filtration yielding 15 mL of a 0.219 M solution of $[(thf)_4CaBr(CH_2SiMe_3)]$ (**3a**) in THF (30 % yield by acidimetric titration). The solvent was removed and the residue was dissolved in 5 mL of THP. This procedure was repeated 3 times. Finally, the remaining white solid was dissolved in 5 mL of THP and 15 mL of pentane. The solution was cooled to – 40 °C, yielding crystals of $[(thp)_4CaBr(CH_2SiMe_3)]$ (**3b**). The crystalline solid was collected, yielding 781 mg of **3b** (1.4 mmol, 13 %), which easily loses coordinated thp during the isolation. Therefore, no reliable combustion analysis data could be obtained. ^{1}H NMR ($[D_8]$THF, 400.13 MHz): δ = -1.83 (s, 2H), -0.13 (s, 9H), 1.53 (m, 16 H), 1.63 (m, 8H), 3.57 (t, 16 H, J = 5.14 Hz). $^{13}C\{^1H\}$ NMR ($[D_8]$THF, 100.6 MHz): δ = 4.5, 5.1, 23.5, 26.6, 68.1. Ca content (%): calc. for $[(thp)_{3.5}CaBr(CH_2SiMe_3)]$: 7.8, found: 8.0.

*Synthesis of $[i\text{Pr}_3SiCH_2Ca(thf)_3(\mu\text{-Br})]_2$ (**4**)*: Activated calcium (403 mg, 10.05 mmol, 1.4 equiv.) was suspended in 20 mL of THF. The suspension was cooled to –78 °C before 1.7 g of $i\text{Pr}_3SiCH_2Br$ (6.8 mmol, 1 equiv.) were added. The reaction mixture was shaken for 2h at –40 °C. Then all solids were removed by filtration, yielding 18 mL of a clear 0.263M solution of ***4*** in THF (70 % yield by acidimetric titration). The solution was concentrated to 5 mL and then 20 mL of pentane were added. Cooling to –40 °C yielded a few crystals of **4**. Additional 20 mL of pentane were added and the reaction mixture was stored for one week at –40 °C. The crystalline solid was collected, yielding 413 mg of $[i\text{Pr}_3SiCH_2Ca(thf)_3(\mu\text{-Br})]_2$ (0.4 mmol, 12 %), which easily loses coordinated THF during handling and isolation. ^{1}H NMR ($[D_8]$THF, 400.23 MHz): δ = -2.26 (br s, 2H), 0.71 (sept, 3H, 7.36 Hz), 0.92 (d, 18 H, 7.36 Hz), 1.71 (m, 12 H), 3.57 (m, 12 H). $^{13}C\{^1H\}$ NMR ($[D_8]$THF, 100.6 MHz): δ = -10.5, 11.9, 17.5, 23.5,

65.4. $^{29}Si\{^1H\}$ NMR ([D$_8$]THF, 79.5 MHz): δ = 10.6. Ca content (%): calc. for [*i*Pr$_3$SiCH$_2$Ca(thf)$_{2.3}$(μ-Br)]$_2$: 8.7, found: 8.6.

*Synthesis of [Me$_3$SiCH$_2$Ca(thf)$_3$(μ-Cl)]$_2$ (**2c**)*: KCH$_2$SiMe$_3$ (358 mg, 2.76 mmol, 1 equiv.) , containing LiCl and/or KCl from the direct synthesis of LiCH$_2$SiMe$_3$ from ClCH$_2$SiMe$_3$ and lithium, were dissolved in 5 mL of THF at 0 °C. To this solution, 14.2 mL of a 0.195M solution of [(thf)$_4$CaPhI] (2.76 mmol) in THF were added dropwise. The white suspension was stirred for 30 min. Afterwards, all solids were removed by filtration, leading to an orange solution. The volume was reduced to 7 mL and additional 7 mL of pentane were added. The solution was stored at –40°C, leading to quantitative precipitation of [(thf)$_4$CaPh$_2$] beneath a few crystals of [Me$_3$SiCH$_2$Ca(thf)$_3$(μ-Cl)]$_2$, which only allow the determination of the crystal structure as well as the ^{1}H-NMR spectrum of this compound. The $^{13}C\{^1H\}$ NMR spectrum shows only the singlet of the methyl-groups. The analysis of the latter solution verified that only chloride counterions are present and no other halides. Due to cocrystallization of [(thf)$_4$CaPh$_2$] no analytically pure product was obtained. ^{1}H NMR ([D$_8$]THF, 300.13 MHz): δ = -1.85 (s, 2H), -0.14 (s, 9H), 1.80 (m, 12 H), 3.64 (m, 12H). $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 75.4 MHz): δ = 4.5, 25.4, 67.2.

*Synthesis of [(pmdeta)Ca{N(SiMe$_3$)$_2$}(CH$_2$SiMe$_3$)] (**5b**)*: KN(SiMe$_3$)$_2$ (293 mg, 1.47 mmol, 1 equiv.) was dissolved in 5 mL of THF. To this solution 21 mL of a 0.07M tetrahydropyran solution of [(thp)$_4$Ca(CH$_2$SiMe$_3$)I] (**3a**, 1.47 mmol, 1 equiv.) were added at 0 °C. The suspension was stirred for half an hour. Then 0.33 mL of PMDETA were added. All volatiles were removed in vacuum and the residue was extracted with 20 mL of pentane. All solids were removed by filtration and the volume of the colorless solution was reduced to 5 ml. Storing at –40 °C led to precipitation of 180 mg of crystalline **5b** (28 %). ^{1}H NMR ([D$_6$]benzene, 300.13 MHz): δ = -1.37 (s, 2H), 0.37 (s, 18H), 0.42 (s, 9 H), 1.38 (m, 4H), 1.64 (s, 3H), 2.00 (m, 4H), 2.13 (s, 12H). $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 100.6 MHz): δ = 6.0, 6.2, 6.7, 45.7, 47.7, 55.5, 56.9. Ca contente (%): calc. for [(pmdeta)Ca{N(SiMe$_3$)$_2$}(CH$_2$SiMe$_3$)]: 8.7, found: 8.5.

Structure Determinations: The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.[42-44] The crystal structures were solved by Direct Methods (SHELXS[45]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97[45] and SHELXL-2014[46]). The hydrogen atoms bonded to the methylene-groups were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen, non-disordered atoms were refined anisotropically.[45,46] The crystal of **2c** contains large voids, filled with disordered solvent molecules. The size of the voids are 271 Å^3/unit cell. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON[47] resulting in 101 electrons/unit cell. Crystallographic data as well as structure solution and refinement details are summarized in Table S1 in the Supporting Information. XP (SIEMENS Analytical X-ray Instruments, Inc.)[48] was used for structure representations.

Computational details: All DFT calculations presented in this study were performed using the Gaussian 16 program.[49] The geometry optimizations of the studied mono radical anions were performed at B97D3 level of theory with the basis set 6-311++G** for all atoms except iodine which was described by the relativistic core potential MWB and the corresponding basis set. Frequency analysis showed no imaginary frequencies.

Supporting Information available

NMR spectra, crystallographic and structure refinement details. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1825811 for **3b**, CCDC-1825812 for **4**, CCDC-1825813 for **2c**, and CCDC-1825814 for **5b**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

The authors declare no conflict of interest.

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Table of Contents Entry

The success of the direct synthesis of heavy *Grignard* reagents, i.e. organocalcium iodides, strongly depends on the C-I bond length of the organyl iodide radical anion that forms after the initial SET reaction, yielding either R-Ca-I and/or *Wurtz*-type C-C coupling products.