Grignard Reagents

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Synthesis of 2,4,6-Trimethylphenylcalcium Iodide and Degradation in THF Solution**

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In contrast to the alkyl- and arylmagnesium halides prepared by Grignard by direct synthesis more than a hundred years ago, the organometallic chemistry of the heavier alkalineearth metals has received little attention.^[1] The main reasons for this are the difficult preparation and the high reactivity of the resulting organometallic compounds. On the one hand, calcium, strontium, and barium metals are not very reactive and must be activated prior to use. On the other hand, the organometallic derivatives tend to cleave ether. Furthermore, owing to the highly ionic metal–carbon bonds these compounds often are insoluble in common organic solvents. In order to overcome these problems several preparative procedures have been developed.^[1,2] The main access routes to organocalcium compounds are:

- 1) the reaction of halogenated hydrocarbons with calcium vapor (cocondensation reaction),^[3,4]
- 2) the insertion of calcium into a carbon-halogen bond in solution (direct synthesis),^[5]
- the substitution of a less electropositive metal by calcium (transmetalation),^[6,7]
- the deprotonation of H-acidic hydrocarbons by calcium or calcium compounds (metalation),^[8]
- 5) the reaction of a organopotassium compound with anhydrous CaI_2 (metathesis reaction).^[9,10]

Beckmann described the synthesis of phenylcalcium iodide in 1905; he applied the direct synthesis in diethyl ether and activated the alkaline-earth metal with a trace of iodine.^[11] More than 80 years later the synthesis of diphenylcalcium in THF at -20 °C was reported by Bickelhaupt and co-workers.^[12] However, neither yields nor physical data were presented. These phenylcalcium compounds were characterized and identified by derivatization, for example, by hydrolysis or reactions with aldehydes, ketones, esters, vinylalkynes, or chlorostannanes followed by hydrolytic workup procedures.

Neither reliable spectroscopic data nor structural parameters of the heavy Grignard reagents have been published.

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Communications

Even less is known about substituted phenylcalcium halides, although several alkyl^[4,9,10] and alkynyl derivatives^[8] have been structurally investigated. However, a very recent success was achieved with the complexes [$F_5C_6M(Ar'-NNN-Ar'']$ by pentafluoro substitution of the phenyl group and by shielding of the reactive M–C bond with the bulky aryl substituents Ar' and Ar''. As a result of the small coordination number of 3 for calcium, a short Ca–C bond of 250(1) pm was observed.^[13] Here we present the first structural proof of a simple heavy Grignard reagent and investigations concerning its high reactivity.

The reaction of iodo-2,4,6-trimethylbenzene (mesityl iodide) with activated calcium metal at low temperatures in THF quantitatively yielded colorless 2,4,6-trimethylphenyl-calcium iodide (1) [Eq. (1)]. When the solution was warmed



above 0 °C it turned yellow, and even at -20 °C a slow color change occurred. After addition of D₂O to the yellow solution, mesitylene with the deuterium atom in a methyl group was observed, which suggests the formation of 3,5dimethylbenzylcalcium iodide according to Equation (2). In



order to verify the rearrangement reaction we examined the reaction at 0 °C by NMR spectroscopy. The intensity of the signals of 1 decreased and finally disappeared, and at the same time signals of 1,3,5-trimethylbenzene (mesitylene) and 3,5-dimethylbenzyl groups appeared and increased in intensity. Mesitylene originated from the ether cleavage reactions already reported for the bis(trimethylsilyl)amides of barium.^[14]

To verify the formation of 2 we performed the direct synthesis with 3,5-dimethylbenzyl bromide and calcium. Compound 2 was obtained in a poor yield of approximately 15%, and bis(3,5-dimethylphenyl)ethane originating from the Wurtz-type coupling reaction was the major product. The NMR data of this benzyl derivative and of 2 were identical.

The high stability of benzylcalcium compounds as a result of the delocalization of the anionic charge was demonstrated earlier.^[10] Mesityllithium,^[15] dimesitylberyllium,^[16] and dimesitylmagnesium^[17] are known. However, only mesityllithium undergoes a similar rearrangement, which was observed above -10°C in a THF solution with formation of 3,5dimethylbenzyllithium.^[18] In pentane in the absence of THF such rearrangement reactions were not observed.^[19]

To clarify the mechanism of this rearrangement, we isolated compound **1** was isolated and dried it under vacuum; the resulting colorless powder was then redissolved in $[D_8]$ THF. In a 2.0 M solution the decomposition was much slower by a factor of approximately 5 to 8, which indicates the involvement of the THF ligands in the rearrangement process. Accordingly the first reaction step is the deprotonation of THF^[20] by the mesityl group (formation of C₆H₃-1,3,5-Me₃). The intermediate α -deprotonated THF can either undergo intramolecular ether cleavage or, in a less favored reaction, remetalate the mesitylene at a methyl group (formation of the 3,5-dimethylbenzyl anion) [Eq. (3)]. The ratio of the 3,5-



dimethylbenzyl to the ether-cleavage products is approximately 1:5. The large effect of the deuterium on the reaction rate suggests that the deprotonation of THF is much slower than the protonation of mesitylene or the ether-cleavage reaction. These investigations indicate that a simple 1,3-H shift within the mesityl group is unlikely.

The molecular structure of 1 is represented in Figure 1. The phenyl group and the iodide are in a *trans* arrangement (C1-Ca-I 177.4(1)°). The mesityl substituent is slightly dis-



Figure 1. Molecular structure of 1 in the crystal (ellipsoids at a probability level of 40%, hydrogen atoms omitted for clarity). Selected bond lengths (pm): Ca–I 320.84(9), Ca–C1 257.4(4), Ca–O1 240.2(3), Ca–O2 240.9(3), Ca–O3 239.3(3), Ca–O4 241.9(3).

torted: The *ipso* carbon atom C1 is pulled out of the plane of the phenyl group, thus leading to an elongation of the C1–C2 (140.2(7) pm) and C1–C6 bonds (143.2(6) pm) as well as a narrow C2-C1-C6 angle of only 114.2(4)°. This fact can be explained by the high ionicity of the Ca–C bond and by the enhanced spatial demand of the {CaI(thf)₄ moiety compared to that of the bonding electron pairs of the *ortho* methyl groups. Similar distortions are a common feature in highly ionic aryl compounds and have also been observed for [(thf)₂Li-C₆H₂-2,4,6-Me₃]₂.^[15] The Ca–C bond length compares well with those of other organocalcium compounds, taking the importance of the coordination number of Ca and the bulk of the substituents into account (Table 1). In [Ca₄(µ₄-O)(C₆H₃-2,6-(OMe)₂)₆], in which the aryl groups bridge the

Table 1: Comparison of Ca-C bond lengths of selected organocalcium compounds.

	CN (Ca) ^[a]	Ca–C [pm]	Ref.
$[Ca{C(SiMe_3)_3}_2]$	2	246	[9]
$[F_5C_6$ -Ca(Ar'-NNN-Ar'')] ^[b]	3	250	[13]
$[(diox)_2Ca(CH(SiMe_3)_2)_2]^{[b]}$	4	248	[4]
$[(thf)_4Ca(CH_2Ph)_2]$	4	258	[10c]
$[(thf)_2Ca(C(SiMe_3)_2Ph)_2]$	4	265	[10a]
$[Mes-Cal(thf)_4]$ (1) ^[b]	6	257	
$[{(thf)Ca-O-C_6H_4-CH-PPh'_2)}_4]^{[b]}$	6	259	[21]
$[(thf)_4Ca(CH(SiMe_3)(C_6H_4-NMe_2)_2]$	6	263	[10b]
[([18]crown-6)Ca(C≡C-SiPh₃)₂]	8	254	[8b]
$[(thf)_2Ca(Me_3Si\text{-}(CH)_3\text{-}SiMe_3)_2]^{[c]}$	8	265	[22]

[a] Coordination number of calcium. [b] Ar': C₆H₃-2,6-Mes₂; Ar'': C₆H₄-2-(C₆H₂-2,4,6-iPr₃); Mes: 2,4,6-trimethylphenyl, mesityl; diox: 1,4-dioxane; Ph': *p*-tolyl. [c] Bis[1,3-bis(trimethylsilyl)allyl]calcium complex.

edges of an oxygen-centered Ca_4 tetrahedron, longer Ca-C bonds between 271.6(4) and 278.5(4) pm were observed.^[23]

In the molecular structure the two THF ligands containing O1 and O3 are bent towards the iodine atom as a result of the steric repulsion between these fragments and the *ortho* methyl groups of the mesityl substituent. In addition, these ligands are turned toward the CaO_4 plane, whereas the other THF molecules are oriented propellerlike to this plane.

The THF complex of 2,4,6-mesitylcalcium iodide is the first example of an isolated and structurally characterized heavy Grignard reagent. The easy access of this highly reactive compound, which can be handled at very low temperatures, could give new impetus to the yet unknown organometallic chemistry of the heavy alkaline-earth metals. In addition we could elucidate the steps of the degradation reaction and show that rather than an intramolecular 1,3-H shift a sequence of deprotonation of THF and subsequent deprotonation of mesitylene leads to the benzyl anion.

Experimental Section

All manipulations were carried out under an anhydrous argon atmosphere. The solvents were thoroughly dried and distilled under an argon atmosphere.

Synthesis of $[MesCaI(thf)_4]$ (1): A 500-mL Schlenk flask containing glass balls (diameter 5 mm), activated calcium (1.84 g, 45.9 mmol), and 90 mL of THF was cooled to -78 °C. Iodo-2,4,6-trimethylbenzene (7.5 g, 30.9 mmol) was added, and the flask was shaken for 5 h. During this time the temperature was kept below -50 °C. The glass balls and the excess calcium metal were removed at temperatures below -30 °C, and the filtrate (90% yield of organo-calcium compound calculated by acid consumption of an aliquot) was stored overnight at -78 °C. The colorless precipitate of **1** (3.46 g, 6.0 mmol, 19.4%) was collected on a cooled frit and dried in vacuo.

Crystalline **1** decomposes above -10° C, whereas in solution decomposition was observed already above -30° C. Compound **1** shows excellent solubility in aromatic hydrocarbons and ethers. In the ¹H NMR spectra at 250 K there are two sets of signals for the mesityl group in a molecular ratio of 3:2 most probably due to a Schlenk equilibrium which gives MesCaI and CaMes₂. Above 310 K only one set of resonances is detected. ¹H NMR (200.1 MHz, [D₈]THF, 250 K): $\delta = 2.02$ (3H, s, *p*-CH₃), 2.24 (6H, s, *o*-CH₃), 6.36 ppm (2H, s, *m*-CH) and the second set: $\delta = 2.04$ (3H, s, *p*-CH₃), 2.31 (6H, s, *o*-CH₃), 6.38 ppm (2H, s, *m*-CH); ¹³Cl¹H} NMR (50.3 MHz, [D₈]THF, 250 K): $\delta = 21.6$ (*p*-CH₃), 27.7 (*o*-CH₃), 124.2 (*m*-CH), 131.0 (*p*-C), 147.1 (*o*-C), 182.5 ppm (*i*-C) and the second set: $\delta = 21.7$ (*p*-CH₃), 28.2 (*o*-CH₃), 123.7 (*m*-CH), 131.1 (*p*-C), 146.6 (*o*-C), 183.0 ppm (*i*-C).

Rearrangement of **1**: An NMR tube containing a solution of **1** in $[D_8]$ THF and THF (molar ratio 10:1) and benzene as a internal standard was kept in a NMR spectrometer at 273 K. The reaction course was followed by NMR spectroscopy. The colorless solution turned more and more yellow as **2** formed. ¹H NMR (200.1 MHz, $[D_8]$ THF, 250 K): $\delta = 1.40$ (2H, s, Ca-CH₂), 1.90 (6H, s, *m*-CH₃), 5.48 (1H, s, *p*-CH), 5.99 ppm (2H, s, *o*-CH); ¹³C{¹H} NMR (50.3 MHz, $[D_8]$ THF, 250 K): $\delta = 22.9$ (*m*-CH₃), 41.2 (CH₂-Ca), 112.1 (*p*-CH), 118.0 (*o*-CH), 136.2 (*m*-C), 160.2 ppm (*i*-C).

Deuterolysis of **2** with D₂O: One-tenth of the filtrate of compound **1** was stirred overnight in an ice bath. The solution turned yellow. The volatile components of the reaction mixture were removed in vacuo, and the residue was treated with 1.0 mL of D₂O and 1.5 mL of CDCl₃ were added. The organic layer was separated and examined by ¹³C NMR spectroscopy. ¹³C{¹H} NMR (50.3 MHz, CDCl₃): $\delta = 20.7$ (t, ¹*J*(¹³C,D) = 19.5 Hz, CH₂D), 21.0 (CH₃), 126.8 (CH), 137.5 ppm (C).

X-ray structure determination of **1**: The intensity data was collected on a Nonius Kappa CCD diffractometer using graphitemonochromated $Mo_{K\alpha}$ radiation. Data was corrected for Lorentz polarization and for absorption effects.^[24-26] The structure was solved by direct methods (SHELXS^[27]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97^[28]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms except for the solvent molecules were refined anisotropically.^[28] XP (SIEMENS Analytical X-ray Instruments, Inc.) and POVRAY were used for structure representations. Crystal data for $\mathbf{1}:^{[29]}$ C₂₅H₄₃CaIO₄·0.75 C₄H₈O, M =

Crystal data for $1^{(2^{\circ})}$ $C_{25}H_{43}CalO_4 \cdot 0.75 C_4H_8O$, $M = 628.65 \text{ gmol}^{-1}$, colorless prism, dimensions $0.05 \times 0.05 \times 0.05 \text{ mm}^3$, monoclinic, space group $P2_1/c$, a = 17.4431(6), b = 13.1064(5), c = 16.9127(7) Å, $\beta = 116.183(2)^{\circ}$, V = 3469.8(2) Å³, $T = -90^{\circ}$ C, Z = 4, $\rho_{calcd.} = 1.203 \text{ g cm}^{-3}$, $\mu(Mo_{K\alpha}) = 10.98 \text{ cm}^{-1}$, multiscan, transmission min.: 0.9426, transmission max.: 0.9778, F(000) = 1312, 24085 reflections in h(-22/22), k(-17/15), l(-21/20), measured in the range $2.68^{\circ} \le \theta \le 27.48^{\circ}$, completeness $\theta_{max} = 99.7^{\circ}$, 7917 independent reflections, $R_{int} = 0.044$, 5342 reflections with $F_o > 4\sigma(F_o)$, 312 parameters, 0 restraints, $R1_{obs} = 0.060$, $wR_{all}^2 = 0.196$, GOOF = 1.036, largest difference peak and hole: $1.328/-1.148 \text{ e} \text{ Å}^{-3}$.

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