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Radical Reactions

Hunting for the Magnesium(I) Species: Formation, Structure, and Reactivity of some Donor-Free Grignard Compounds**

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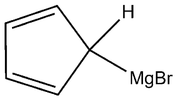
Dedicated to Professor Dieter Fenske on the occasion of his 70th birthday

In analogy to and as a consequence of our previous work, starting with the generation of Al^I/Ga^I halides[1] and ending up with the formation of metalloid aluminum and gallium clusters as intermediates between the bulk element and salt-like compounds,[2] we have been interested in investigating the monovalent state of Mg as the neighbor element of Al, and in particular thermodynamic and quantum chemical considerations.[3] However, as the generation of MgCl for example is much more difficult than the formation of AlCl,[4] we worked intensively to develop suitable experimental methods for the generation of MgCl. During this time, low-valent Group 2 element chemistry has been developed[5] and the groups of Jones and others[6,7] were successful in presenting first examples of molecules that contain Mg^I atoms within an Mg–Mg σ bond stabilized by chelating ligands to each Mg center: [RMgMgR] ($R = [(Ar)NC(N\textit{i}Pr_2)N(Ar)]^-$(priso) and $[\{(Ar)NCMe\}_2CH]^-$(nacnac); Ar = 2,6-diisopropylphenyl, *i*Pr = isopropyl). In contrast to these unexpectedly kinetically stable compounds, we were interested in more simple and more reactive species in which the ligands R are directly σ-bonded to the Mg center. Therefore we decided first to develop a classical synthesis of $[(MgR)_n]$ species containing organic ligands R by the reduction of donor-free Grignard compounds.

We decided to start with $[(MgCp^*X)_n]$ compounds (X = halides), as the first classical synthesis of AlCp* and GaCp*[8–10] also started with normal valent dimeric $[AlCp^*X_2]$ and $[GaCp^*X_2]$ molecules.[11,12]

However, the preparation of donor-free Grignard compounds is not an easy task, as we have already shown with the formation of an $[Mg_6Cl_8Cp^*_5]^-$ anion that is stabilized in the lattice by the large, weakly coordinating and stable aluminocenium cation $[AlCp^*_2]^+$.[13] As the formation of this compound is a byproduct during the Cp* transfer from $[MgCp^*_2]$ to the metastable AlX solution, we developed an improved method: equivalent amounts of $[MgCp^*_2]$ react with $[Cp^*AlX_2]$ in toluene; that is, without a donor compound. Using this method, we obtained the following three donor-free oligomeric anionic Grignard compounds, which are stabilized each with $[AlCp^*_2]^+$ cations in a solid lattice: $[AlCp^*_2]^+[Mg_3Cl_4Cp^*_3]^-$ (**1**), $[AlCp^*_2]^+[Mg_6Br_8Cp^*_5]^-$ (**2**), and $[AlCp^*_2]^+[Mg_2I_3Cp^*_2]^-$ (**3**). These three compounds are shown in Figure 1 along with the most important structural parameters.[14] All of the MgX and MgCp* distances are in accordance with expectations.

Particularly fascinating for our final aim of an Mg^I species is the structure of the $[Mg_2I_3Cp^*_2]^-$ anion (**3**), which corresponds to the neutral $[Cp^*MgI_2MgCp^*]$ species. Such a molecule is interesting for two reasons: 1) it is a donor-free dimeric [CpMgX] species (Scheme 1) that was already mentioned by Grignard in 1912;[15] and more importantly for our purposes, 2) the arrangement of the two halide-bridged Mg atoms should make a classical formation of an Mg–Mg bond possible by a reduction process such as that mentioned above for $[Cp^*XAlX_2AlXCp^*]$.[11] However, though we made several attempts to remove the halides of **1** and **2** with Na/K alloys under various soft conditions, we were not able to avoid the reduction to elemental magnesium; that is, it was not possible to trap the desired $[Cp^*MgMgCp^*]$ molecule, which has been predicted to be a metastable molecule with a large HOMO–LUMO gap (ca. 4 eV) by DFT calculations.[16] Therefore, a classical synthesis of compounds containing Mg–Mg bonds that are not stabilized by chelating ligands seems to be difficult, and perhaps impossible.



Scheme 1. The structure of [CpMgBr] proposed by Grignard.

Consequently, we had to use an experimentally more sophisticated route via the preparation of the high-temperature molecule MgCl and its trapping in a metastable

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Supporting information for this article, including experimental details, quantum chemical calculations, thermodynamic investigations, and crystallographic details, is available on the WWW under http://dx.doi.org/10.1002/anie.201204997.

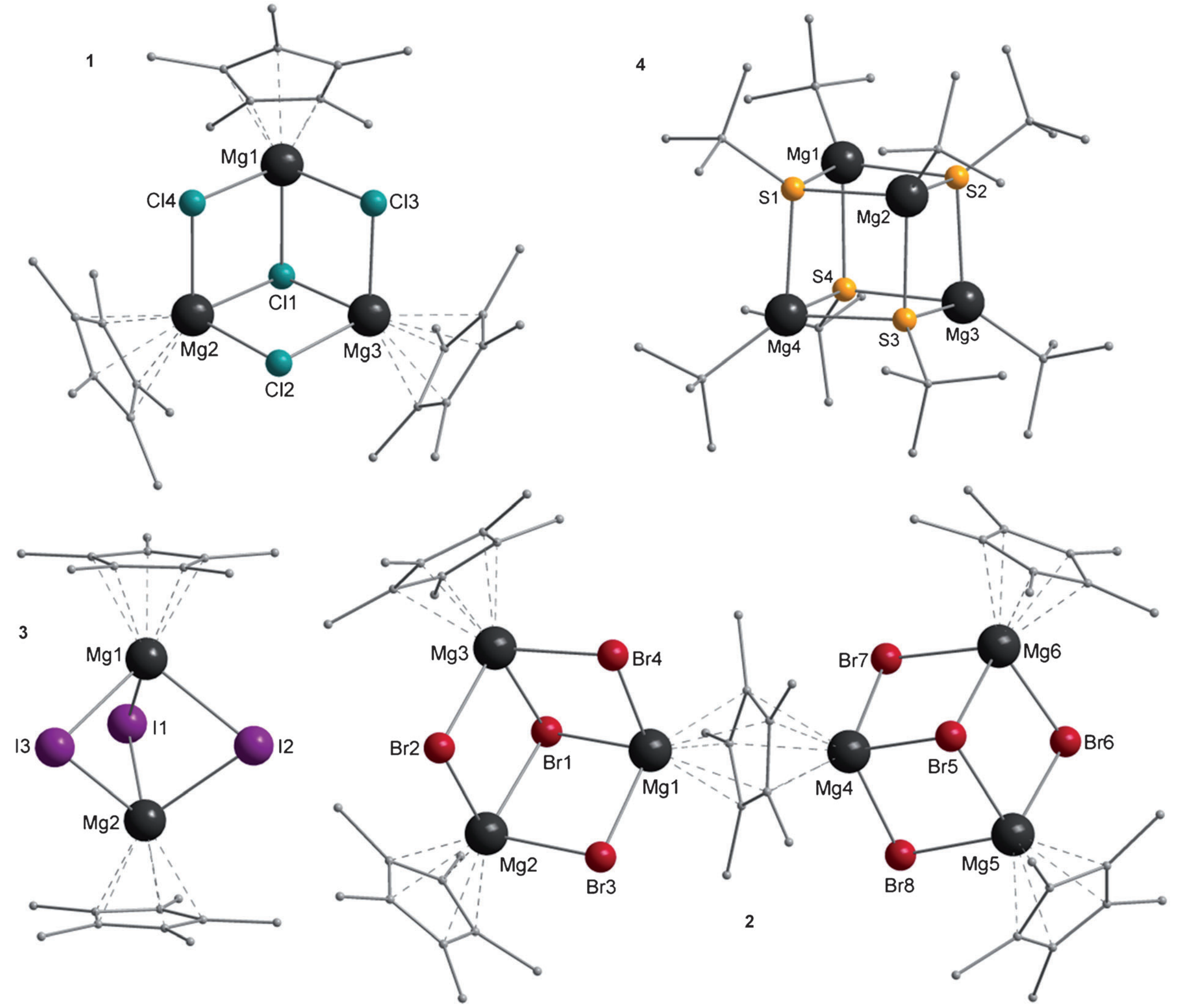


Figure 1. Molecular structures of **1**, **2**, **3** (without $[AlCp^*_2]^+$ cation), and **4** in the crystal (H atoms omitted for clarity). Selected bond lengths and average distances [max/min] [Å]: **1**: Mg–Cl 2.45 [2.583(1)/2.389(1)], Mg–Cp* 2.05 [2.061/2.037]; **2**: Mg–Br 2.61 [2.745(4)/2.516(4)], Mg–Cp* 2.015 [2.022/2.007], Mg–(μ-Cp*) 2.105 [2.110/2.100]; **3**: Mg–I 2.85 [2.882(1)/2.843(1)] Mg–Cp* 2.04 [2.070/2.016]; **4**: Mg–S 2.55 [2.552(2)/2.539(2)], Mg–C 2.13 [2.132(6)/2.121(5)], S–C 1.86 [1.866(7)/1.859(5)].

solution. We first checked the new route with the help of matrix investigations, where MgCl molecules in a milligram scale have been obtained at about 700 °C according to the following reaction:[17]

$$2\,MgB_{2(s)} + HCl_{(g)} \rightleftharpoons MgCl_{(g)} + \tfrac{1}{2}\,H_2 + MgB_{4(s)}{}^{[18]} \qquad (1)$$

The MgCl radicals easily dimerize in the solid matrix of argon to the classically bonded [ClMgMgCl] molecules, which have been detected by their resonance Raman spectrum. From the overtones of the Mg–Mg vibration, the dissociation energy could be determined to be about 200 kJ mol^{-1}, which is in accordance with theory.[17]

We then enlarged our MgB_2 based synthesis from the matrix experiments with the same apparatus which has been applied for all our AlX/GaX preparations:[1c] only the reactor has been changed; it contains MgB_2 instead of Al/Ga, which reacts with HBr to $MgBr_2$ and MgB_4[19] at about 850 °C (Figure 2). However, the primarily formed $MgBr_2$ molecules subsequently react with the solid MgB_4, and a mixture of gaseous $MgBr_2$ and MgBr molecules is obtained in the gas phase, as predicted by theory and thermodynamic considerations (see the Supporting Information).[20] The trapped metastable solution (toluene/donor molecules = 23:1) of MgBr/$MgBr_2$ contains different ratio of Mg^I and Mg^{II} species depending on the experimental conditions: flow speed of HBr, ratio of solvent/donor (mostly NEt_3 or PEt_3), and ratio of MgBr to solvent molecules.

In any case, all of the homogenous solutions very easily disproportionate to form an Mg mirror on the walls of the glass vessel at temperatures higher than −40 °C. Therefore, we have not yet been successful in crystallizing a highly sensitive magnesium subhalide compound. To confirm the presence of MgBr molecules chemically, we substituted the halide by the halide-like SR^- anion. With the bulky *t*Bu ligand, a [MgS*t*Bu] radical or a dimeric or oligomeric species was expected.[21]

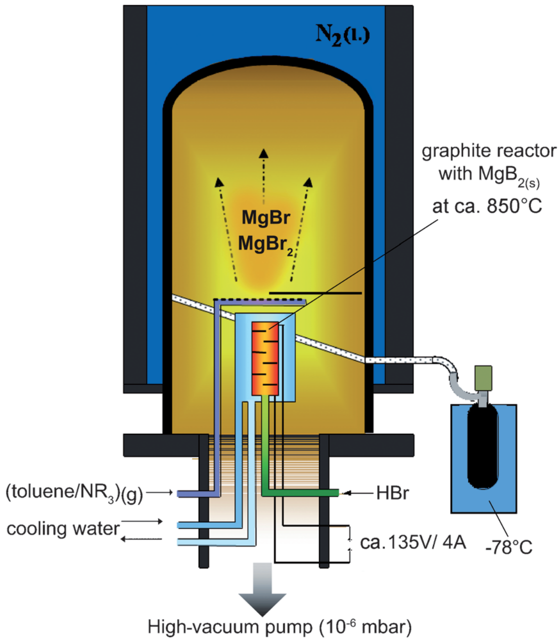


Figure 2. The co-condensation apparatus.

However, we observe the following: 1) the dark brown color of the extracted homogeneous reaction solution (MgBr + Li*St*Bu) in pentane disappears within a few days; 2) colorless crystals of the Grignard-like [(*t*BuMgS*t*Bu)$_n$] compounds appear, namely [{(*t*Bu)Mg(S*t*Bu)}$_4$] (**4**) (Figure 1) and [(*t*Bu)$_3$Mg$_3$(S*t*Bu)$_4$Li(N*n*Bu$_3$)] (**5**) (for the crystal structure, see the Supporting Information);[22,23] and 3) concomitantly, a strong broad EPR signal decreases to a very small one.[24]

Obviously a redox reaction has occurred in which the *t*Bu$^+$ unit in the S*t*Bu$^-$ moiety is reduced to *t*Bu$^-$, which then is directly connected to the oxidized Mg^{2+} cation; that is, the SR$^-$ anion could react like the isoelectronic RCl species in a Grignard-like formation reaction with elemental magnesium.[25]

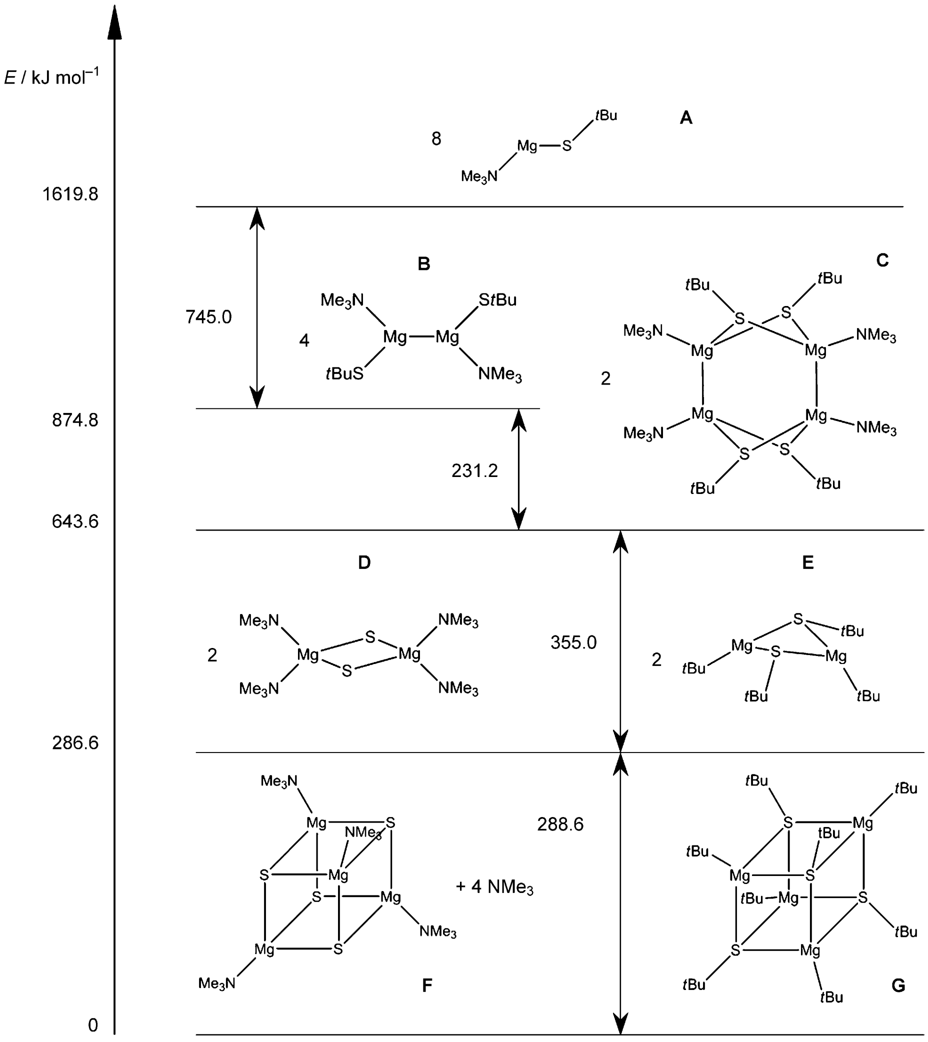
However, as no metallic magnesium is formed in our case, the reaction proceeds via MgBr radicals or oligomeric MgBr species. After the substitution reaction of MgBr with LiSR species, LiBr oligomers (LiBr indentified by X-ray powder diffraction) and MgSR radicals are formed. The latter pathway favors a redox reaction [Eq. (2)] to oligomeric MgS and the tetrameric donor-free Grignard-like compound [(RMgSR)$_4$] (**4**).

$$\begin{array}{l} 8\,\mathrm{MgBr} + 8\,\mathrm{LiSR} \rightarrow 4\,\mathrm{MgS}\boxed{\mathrm{R}^{\bullet} + 4\,\mathrm{MgSR}^{\bullet}} + 8\,\mathrm{LiBr} \\ \qquad\qquad\qquad\qquad\quad \downarrow \qquad\quad \downarrow \\ \qquad\qquad\qquad\quad (\mathrm{MgS})_4 + (\mathrm{RMgSR})_4 \end{array} \qquad (2)$$

Finally, **5** is formed with an excess of Li(SR) [Eq. (3)].

$$6\,\mathrm{Mg(SR)} \rightarrow [\mathrm{R_3Mg_3(SR)_3}] \xrightarrow{\mathrm{Li(SR)}} [\mathrm{R_3Mg_3(SR)_4}]\mathrm{Li}\ (\mathbf{5}) + 3\,\mathrm{MgS} \qquad (3)$$

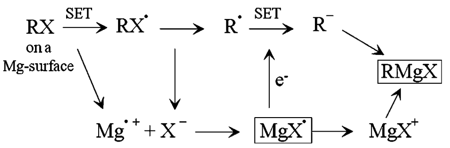
This simplified principal reactivity has been verified more convincingly with DFT calculations; the results are summarized in Scheme 2. Starting from 8[Mg(SR)$^{\bullet}$] (R = *t*Bu) radicals (**A**) stabilized by NMe$_3$ donor species by four dimeric intermediates [(NMe$_3$)(RS)Mg-Mg(SR)(NMe$_3$)] (**B**),[26,27] two tetrameric species **C** are formed with a structure analogous to the [Mg$_4$Cl$_4$] species published earlier.[3] Thereafter two Mg$_2$ moieties are formed ([(MgS)$_2$] (**D**) and [(RMgSR)$_2$] (**E**)) via a redox process, and finally the products **F** and **G**, that is, a tetrameric donor-stabilized MgS and a tetrameric Grignard-like compound similar to **4**, are obtained exothermically.



Scheme 2. Energy diagram (from DFT calculations) of the reaction of Li*St*Bu with MgBr.

Thus, our investigations have shown that 1) donor-free Grignard compounds with non-chelating ligands cannot be reduced to $\mathrm{Mg^I}$ compounds without decomposition to elemental Mg: either the exothermic reduction with Na/K alloys cannot be interrupted, or the $\mathrm{Mg^I}$ intermediate disproportionates at the reaction temperature;[28,29] and 2) a sophisticated procedure is necessary to generate and to trap MgBr high-temperature species. Their formation was confirmed experimentally using a) the disproportionation of the trapped metastable dark brown MgBr solutions and the formation of an Mg mirror inside the Schlenk vessel while the EPR spectrum of the original MgBr solution and the brown color disappear simultaneously; and b) a redox reaction of the primarily formed $[\mathrm{Mg(SR)}^\bullet]$ radicals formed after the substitution of $\mathrm{Br^-}$ by $\mathrm{SR^-}$ ends up with a Grignard-like compound $[\{\mathrm{RMg(SR)}\}_4]$ (**4**).

The results presented herein provide experimental evidence to the mechanism of the formation of Grignard compounds via two single electron transfer steps (SET) and the presence of radicalic magnesium subhalides as intermediates. Thus, some progress has been made in the understanding of one of the most famous reactions in organic chemistry; as the detailed mechanism of formation still needs to be fully clarified more than 100 years after its detection.[15,30] In ongoing experiments, we are focusing on the isolation and also structural and reactivity investigations of low-valent magnesium halides to confirm the results presented herein.



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[14] An $[\mathrm{AlCp^*_2}]^+[\mathrm{Mg_6Cl_6Cp^*_5}]^-$ compound (**2a**) that contains toluene as solvent has been obtained; this anion is identical to our previously published species.[13] These magnesiate species **1**, **2**, and **3** are different from the well-known dimetallic ate complexes with their high potential in synthetic organic chemistry: R. E. Mulvey, F. Mongin, M. Uchiyama, Y. Kondo, *Angew. Chem.* **2007**, *119*, 3876; *Angew. Chem. Int. Ed.* **2007**, *46*, 3802.

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[18] $\mathrm{MgCl_2}$ molecules that are formed simultaneously react in a subsequent reaction with the generated $\mathrm{MgB_4}$ solid: $\mathrm{MgB_4 + MgCl_2 \rightleftarrows 2\,MgCl + 4\,B}$ (see the Supporting Information).

[19] $\mathrm{MgB_4}$ as a product has been characterized by powder X-ray diffraction.

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[21] A tetrameric, donor-stabilized $[\mathrm{Mg_4(S}t\mathrm{Bu)_4{\cdot}4\,L}]$ molecule has been proposed, which should have the similar structure as a $[\mathrm{Mg_4Cl_4}]$ containing two MgMg σ bonds and two $\mathrm{MgCl_2Mg}$ bridges (compare with Scheme 2, compound C).[3]

[22] In contrast to other examples of $[(\mathrm{RMgSR})_n]$ species that have been presented and well characterized,[23] in our redox experiments no $\mathrm{MgR_2}$ moieties are present in the starting materials, such as $\mathrm{4\,Mg^*Cp_2 + 4\,HSR \rightarrow Cp^*_4Mg_4S_4R_4}$, $\mathrm{R = C(CH_3)}$;[23] that is, compound **4** is not interesting because of its structure but because of its formation.

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[25] This hypothetical reaction should proceed like the formation of Grignard compounds (that is, $RCl + Mg \rightarrow RMgCl$). Compound **4** could be formed by the reactions presented on Equation (4a) and (4b), and $[(t\mathrm{Bu})_3Mg_3(St\mathrm{Bu})_4Li(Nn\mathrm{Bu}_3)]$ (**5**) is finally obtained if an excess of LiSR is applied [Eq. (4c)].

$$Li(RS) + Mg \rightarrow Li(S\text{-}Mg\text{-}R) \qquad (4a)$$

$$4\,Li(S\text{-}MgR) + 4\,Li(SR) \rightarrow 4\,Li_2S + 4\,(R^+ + {}^-SMgR)$$
$$\rightleftarrows 4\,(Li_2S)_n + (RSMgR)_4\ (\mathbf{4}) \qquad (4b)$$

$$7\,Li(SR) + 3\,Mg \rightarrow 3\,Li_2S + [R_3Mg(SR)_4]Li\ (\mathbf{5}) \qquad (4c)$$

Simultaneously, donor-stabilized Li_2S oligomers and finally solid Li_2S should be formed.

[26] This species has an Mg–Mg distance of 287.0 pm; that is, the situation is different from that of the diradicalic $RAl(R_2)AlR$ species.[27] See also the Supporting Information, Figure S4.

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