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The Anion $[Mg_6Cl_8Cp^*_5]^-$: A Final Intermediate on the Way to the Molecular Donor-Free Grignard Compound MgClCp*?

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Summary: The reaction at −70 °C of decamethylmagnesocene $MgCp^*_2$ (Cp = pentamethylcyclopentadienyl) with monovalent aluminum chloride, AlCl, stabilized with diethyl ether and dissolved in toluene, results in tetrameric tetrahedrotetrakis-(pentamethylcyclopentadienylaluminum), $[AlCp^*]_4$, and the dimeric bis(pentamethylcyclopentadienylmagnesium chloride diethyl etherate), $[MgCp^*Cl{\cdot}Et_2O]_2$. At a slightly higher temperature and by stepwise decrease of the diethyl ether concentration before reaction, a preferred formation of metal clusters such as dodekakispentamethylcyclopentadienylpentacontaaluminum, $Al_{50}Cp^*_{12}$, was frequently observed. Interestingly, after working up the residue of this reaction, a new kind of Grignard compound could be isolated. We report here on the synthetic details and X-ray structure of a donor-free Grignard compound with an inverse magnesocene motif, μ-Cp^*Mg_2, in the anionic part of the compound, $[Mg_6Cl_8Cp^*_5][AlCp^*_2]{\cdot}C_6H_6$ (**1**).*

Introduction

Magnesium organyl compounds such as $MgCp_2$[1,2] and $MgCp^*_2$ have proved to be powerful starting materials in synthetic chemistry, although the X-ray structure of $MgCp^*_2$ was determined only recently.[3] For instance, $MgCp^*_2$ was an essential precursor for the preparation of the first Al(I) organic compound $(AlCp^*)_4$ via a substitution reaction of metastable AlCl.[4,5] Since only one Cp* ligand of $MgCp^*_2$ could be transferred to the Al(I) species, in every case the Grignard compound $[MgCp^*X{\cdot}D]_2$ (D = donor solvent)[6] as the donor-stabilized dimer was obtained. To vary the synthesis of AlCp* in favor of the formation of metal clusters,[7] e.g., the $Al_{50}Cp^*_{12}$ cluster,[8] the donor concentration during the reaction must be reduced stepwise via evacuation. This low concentration of, for example, diethyl ether may be the reason for the formation of donor-poor Grignard compounds, i.e., of oligomers in which the low coordination number of magnesium is compensated by self-aggregation and not via classical donor stabilization. Herein we report an example of this kind, a compound containing the donor-free anion $[Mg_6Cl_8Cp^*_5]^-$.

Results and Discussion

A metastable solution of AlCl in an ether−toluene mixture (1:3 v/v)[7] was concentrated in a vacuum, to reduce the amount of ether, at −30 °C. The remaining solution was reacted with $MgCp^*_2$. Measuring a NMR sample of the mixture, a high-shifted NMR signal at − 272 ppm in the ^{27}Al NMR spectra indicates the beginning of cluster formation assigned to the inner shell of $Al_{50}Cp^*_{12}$,[8] but this time only the solid compounds $(AlCp^*)_4$[5] and $(MgCp^*Cl{\cdot}Et_2O)_2$[6] were obtained from the reaction mixture by fractional crystallization. After removal of the remaining solvent in vacuo and extraction of the solid residue with benzene, colorless crystals of $[Mg_6Cl_8Cp^*_5][AlCp^*_2]{\cdot}C_6H_6$ (**1**) were obtained. The crystals of **1** were suitable for X-ray analysis. Compound **1** crystallizes in the orthorhombic space group $P2_12_12_1$ with two molecules per unit cell. The X-ray structure analysis of **1** is presented in Figure 1. Relevant crystallographic data are given in Table 1, with selected bond lengths and angles listed in Table 2.

The anion **1a** contains the heterocubane-like fragment of a donor-free Grignard compound, and the **1b** ion is the sandwich-like aluminocenium cation $[AlCp^*_2]^+$, which we synthesized some years ago.[9] The aluminocenium cation **1b** exhibits structural and NMR parameters very similar to those described earlier.[9] The formation of **1b** is evidence for the internal disproportion process of the metastable AlCl species or AlCp* oligomers as intermediates.

The most remarkable feature of the structure of **1a** is its inverse sandwich-like MgCp*Mg moiety, which, as far as we know, has not been observed for magnesium before, although it is known for other main group elements.[10] This dimerization via a bridging Cp* ligand seems to be favored because of a deficiency of Cp* ligands and magnesium ions in this solution. The same situation is observed for MgX_2 dihalides, when monomeric species with 4-fold-coordinated Mg atoms are present due to the presence of an excess of ether $[MgX_2{\cdot}2D]$ and when solid MgX_2 as an ionic lattice ($CdCl_2$ structure) with

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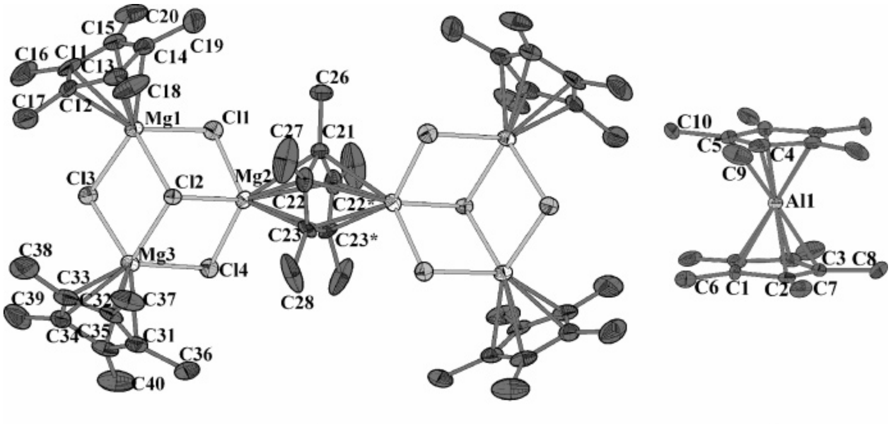

1a **1b**

Figure 1. Molecular structure of $[Mg_6Cl_8Cp^*_5][AlCp^*_2]\cdot C_6H_6$ (**1**)with the anion $[Mg_6Cl_8Cp^*_5]^-$ (**1a**) and the aluminocenium cation $[AlCp^*_2]^+$ (**1b**) (benzene and H atoms are omitted). Thermal ellipsoids are shown at 50%. Average distances [pm] of **1a**: $Mg-C_{ring}$ 237.6, $Mg-\mu$-C_{ring} 242.2, $Mg-Cp_{ringcentroid}$ 205.3, $Mg-\mu$-$Cp_{ringcentroid}$ 211.5, $Mg-\mu^3$-Cl 253.0, $Mg-\mu$-Cl 241.1, μ-$C_{ring}-C_{ring}$ 139.1, $C_{ring}-C_{ring}$ 140.9, $C_{ring}-C_{methyl}$ 151.2. Average distances [pm] of **1b**: $Al-C_{ring}$ 212.4, $Al-Cp_{ringcentroid}$ 172.7, $C_{ring}-C_{ring}$ 145.4, $C_{ring}-C_{methyl}$ 153.1.

Table 1. Crystal Data for 1

compd·solvate	$C_{76}H_{111}AlCl_8Mg_6$
fw	1481.09
temp, K	200(2)
wavelength, Å	0.71073
cryst syst	orthorhombic
space group	$P2_12_12_1$
cryst dimens, mm	0.50 × 0.30 × 0.15
a, Å	15.7808(10)
b, Å	16.3514(13)
c, Å	16.6649(9)
V, Å^3	4300.2(5)
Z	2
d_{calcd}, g cm^{-3}	1.144
abs coeff, mm^{-1}	0.353
F(000)	1576
max 2θ, deg	51.98
index ranges	$-20 \leq h \leq 20$; $-19 \leq k \leq 19$; $-20 \leq l \leq 20$
no. of rflns [R_{int}]	31 907 [0.0546]
no. of indep rflns	8409
no. of data/restraints/params	8409/9/398
goodness of fit on F^2	0.897
final *R* indices ($I > 2\sigma(I)$)	$R_F = 0.0457$, $R_w = 0.1156$
largest diff peak and hole, e Å^{-3}	0.823 and −0.299

Table 2. Selected Bond Lengths [pm] and Angles [deg] for 1

Mg(1)−Cl(1)	251.6(4)	Mg(3)−Cl(4)	251.3(4)
Mg(1)−Cl(2)	254.6(3)	Mg(3)−C(31)	235.0(9)
Mg(1)−Cl(3)	237.7(4)	Mg(3)−C(32)	235.4(10)
Mg(1)−C(11)	239.0(11)	C(21)−C(22)	132.2(10)
Mg(1)−C(12)	241.7(10)	C(22)−C(23)	133.8(11)
Mg(2)−Cl(1)	234.6(3)	C(23)−C(23)*	163.9(13)
Mg(2)−Cl(2)	251.9(1)	C(22)*-C(21)	132.2(10)
Mg(2)−Cl(4)	233.0(3)	C(21)−C(26)	156.2(11)
Mg(2)−C(21)	250.4(5)	C(22)−C(27)	162.7(11)
Mg(2)−C(22)	236.9(8)	C(23)−C(28)	147.2(12)
Mg(2)−C(23)	236.8(8)	Al(1)−C(1)	213.0(9)
Mg(2)−C(22)*	246.1(8)	Al(1)−C(2)	216.6(9)
Mg(2)−C(23)*	240.8(9)	Al(1)−C(3)	209.9(9)
Mg(3)−Cl(2)	252.3(3)	Mg(1)−Mg(2)	351.7(4)
Mg(3)−Cl(3)	238.1(4)	Mg(1)−Mg(3)	361.3(4)
Cl(1)−Mg(1)−Cl(2)	87.1(1)	Cl(2)−Mg(3)−Cl(3)	84.78(9)
Cl(2)−Mg(1)−Cl(3)	84.35(9)	Cl(2)−Mg(3)−Cl(4)	87.1(1)
Cl(3)−Mg(1)−Cl(1)	101.8(1)	Cl(3)−Mg(3)−Cl(4)	101.9(1)
Cl(1)−Mg(1)−C(11)	127.9(3)	Cl(2)−Mg(3)−C(31)	114.3(3)
Cl(1)−Mg(1)−C(12)	154.2(3)	Cl(2)−Mg(3)−C(32)	95.0(2)
Mg(1)−C(11)−C(16)	120.1(7)	Mg(3)−C(31)−C(36)	122.0(6)
Cl(1)−Mg(2)−Cl(2)	91.57(7)	Mg(1)−Cl(1)−Mg(2)	92.6(1)
Cl(1)−Mg(2)−Cl(4)	104.6(2)	Mg(1)−Cl(2)−Mg(2)	87.93(8)
Cl(2)−Mg(2)−Cl(4)	91.23(7)	Mg(1)−Cl(2)−Mg(3)	90.9(1)
Cl(1)−Mg(2)−C(21)	90.09(6)	Mg(1)−Cl(3)−Mg(3)	98.8(2)
Cl(1)−Mg(2)−C(22)	114.0(2)	Mg(2)−Cl(2)−Mg(3)	88.16(8)
Mg(2)−C(21)−C(26)	122.72(5)	Mg(2)−Cl(4)−Mg(3)	92.7(1)

a Mg coordination number of 6 is preferred in the absence of diethyl ether. However, if the amount of diethyl ether is diminished carefully, $[MgX_2\cdot Et_2O]_n$ is observed in which a chain-like structure containing five-coordinate magnesium is present.[11] In the system of $MgCl_2$ and diethyl ether we have recently been successful in obtaining a highly symmetrical $[Mg_3Cl_5\cdot 6Et_2O]^+$ intermediate[12] in which the metal atoms and the five chlorine and six oxygen atoms of the ligands form a structural unit, similar but inverse to that of the metal-rich $Cs_{11}O_3$ suboxide entity.[13]

In **1a** we have a fragment of the thus far unknown structure of a molecular Grignard compound. However, many years ago some results in this field were described by Klabunde,[14] but without structural information. Furthermore, a polymeric chain-like structure containing MgR_2 and MgRBr units has been presented by Bickelhaupt recently.[15] The latter compound is, as far as we know, the only structurally characterized donor-free Grignard-like compound fragment published to date. Further developments in this field were described quite recently by Knochel.[16]

The Grignard-like fragment in **1a** resembles two parts of a heterocubane-like structure. A complete heterocubane structure of this type is present in the valence-isoelectronic molecule $[AlCp^*Se]_4$.[17,18] From this analogy it can be deduced that a compound, e.g., $[MgCp^*Cl]_4$, might exist. Its synthesis may be possible under conditions such as those used for **1**, but with more $MgCp^*_2$ in the solution. A much simpler synthesis of $[MgCp^*Cl]_4$ should be possible starting with the $[MgClCp^*\cdot$

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$Et_2O]_2$ compound mentioned above, performing a dimerization reaction while the diethyl ether is carefully removed. DFT calculations for this process (eq 1) show an energy increase of

$$2\,[MgCp^*Cl\cdot Et_2O]_2 \rightarrow [MgCp^*Cl]_4 + 4\,Et_2O \qquad (1)$$

only 100 kJ·mol^{-1} for the reaction enthalpy $\Delta_R H°$. Because of the increase in $\Delta_R S°$, it seems promising to perform these experiments in order to obtain the first pure molecular donor-free Grignard compound. These experiments are currently ongoing.

Summary

We have prepared and structurally characterized a rare example of a donor-free Grignard compound. The structure of $[Mg_6Cl_8Cp^*_5][AlCp^*_2]\cdot C_6H_6$ (**1**) has been confirmed by X-ray diffraction analysis. Its structure contains the first inverse magnesocene motif in its anionic part. The compound is of special interest in terms of its composition: a normal (Cp*AlCp*) and an inverse (MgCp*Mg) metallocene moiety are both present in one crystalline compound.

Experimental Section

$MgCp^*_2$ was synthesized as described in the literature.[19] A 0.38 M $AlCl\cdot Et_2O$ solution in toluene was prepared using the co-condensation technique described earlier.[7] Benzene, toluene, diethyl ether, and *n*-pentane were dried over sodium, freshly distilled under argon, and freeze−thaw−degassed prior to use. All manipulations were carried out under high-purity nitrogen in flame-dried glassware. The quantum-chemical calculations (DFT) were performed with the TURBOMOLE program package. The BP86 functional with the SVP basis set was used for the elements.[20]

$[Mg_6Cl_8Cp^*_5][AlCp^*_2]\cdot C_6H_6$ (1). The diethyl ether component of a 43 mL portion of a 0.38 M $AlCl\cdot Et_2O$ toluene solution (25 vol % Et_2O, $\omega(AlCl) = 92\%$, 15 mmol) was concentrated to 30 mL in vacuo over a period of 8 h at −50 to −40 °C, and 4.42 g of $MgCp^*_2$ (15 mmol) dissolved in toluene was added to the solution at −70 °C. The resulting dark red reaction mixture was warmed to −30 °C and stirred for 3 h. Subsequently, all volatile components were removed, and the residue was washed with 15 mL of pentane. The residue was extracted with toluene, and after taking a NMR sample the extract was stored at −30 °C. An amount of 1.29 g (1.99 mmol) of yellow crystals of $[AlCp^*]_4$ and 0.51 g (0.95 mmol) of colorless crystals of $[MgCp^*Cl\cdot Et_2O]_2$ were isolated from the toluene extract after several concentrating steps. After removing the rest of the toluene the residue was washed with benzene. After 2 weeks colorless crystals of **1** were obtained from the benzene extract stored at ambient temperature. The sample for NMR spectroscopy was separated from the solution directly after the reaction had been performed.

^{27}Al NMR (78 MHz, C_6D_6, ppm): δ −80 $[\mathit{Al}Cp^*]_4$, −114 $[\mathit{Al}Cp^*_2]^+$, −272 $[\mathit{Al}_8Al_{42}Cp^*_{12}]$. ^1H NMR (250 MHz, C_6D_6, ppm): δ 1.97 (broad). ^{13}C NMR (63 MHz, C_6D_6, ppm): δ 10.7 $[\mathit{Me}_5C_5]$, 111.0 $[Me_5\mathit{C}_5]$.

Crystallographic Analysis for 1. A crystal of **1** was mounted on a glass fiber in silicone oil at −73 °C. The data were collected on a STOE IPDS two-circle diffractometer using graphite-monochromated Mo Kα radiation and a Stoe-IPDS area detector. The data were corrected for absorption by the Stoe IPDS software. Lorentz polarization and absorption corrections were applied. The structural solution (calculated by direct methods) and refinement (on F^2, H atoms calculated) were carried out using the Sheldrick SHELX97 program suite.

CCDC-290653 (**1**) contains the supplementary crystallographic data for this note at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Data for **1** can be obtained free of charge via the Internet at http://pubs.acs.org.

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