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The crystal and molecular structure of pentamethylcyclopentadienyl Grignard reagent: $[Cp^{\star}Mg(thf)\mu\text{-}Cl]_2$

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Abstract

The crystal and molecular structure of pentamethylcyclopentadienyl Grignard reagent has been determined by X-ray diffraction in the monoclinic space group $C2/c$; cell parameters a 21.51(2) Å, b 11.778(6) Å, c 14.04(1) Å, α 90°, γ 90°, β 95.17(7)°, V 3543(5) Å^3, $Z = 4$ dimers, with $R = 0.1047$, $R_w = 0.0938$, $R_G = 0.1068$. The pentamethylcyclopentadienyl Grignard reagent is a dimer in which chloro ligands bridge two Mg^{2+} ions which are each coordinated to a η^5-Cp* group and a THF molecule. A disordered toluene molecule is also found in the crystal lattice.

Introduction

Despite the fact that the cyclopentadienyl magnesium Grignard reagent, CpMgBr, has been known for more than 70 years [1] and that it and its pentamethylcyclopentadienyl analog have been used as reagents in synthetic chemistry, only two structures have been determined for cyclopentadienyl-magnesium halides: $CpMg(Br)(Et_2NCH_2CH_2NEt_2)$ [2] and $[(Me_3Si)_2C_5H_2]Mg(Br)(Me_2NCH_2CH_2NMe_2)$ [3]. In fact, very few Grignard reagents of any type have been structurally characterized. These include several bromo derivatives $PhMg(Br)(OEt_2)_2$ [4], $[EtMg(Br)(NEt_3)]_2$ [5], $[EtMg(Br)(OPr_2)]_2$ [6], $EtMg(Br)(OEt_2)_2$ [7], and $MeMg(Br)(thf)_3$ [8], and a chloro Grignard, $[EtMg_2Cl_3(thf)_3]_2$ [9] ($Cp = C_5H_5$; $Cp^{\star} = C_5Me_5$; $Ph = C_6H_5$; $Et = C_2H_5$; $Me = CH_3$). Here we report the molecular structure of pentamethylcyclopentadienyl magnesium chloride to be the dimeric tetrahydrofuran adduct in the solid state. The structure agrees with that proposed by Marks et al. [10] and is the first crystallographically characterized dimeric chloro Grignard reagent.

Experimental

In our investigations of phosphoylide actinide chemistry [11], we use $Cp^{\star}_2AnCl_2$ (An = Th or U) as a starting material. In the synthesis of this compound we use the pentamethylcyclopentadienyl magnesium Grignard reagent as described in the liter-

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ature [10]. During one experiment the pentamethylcyclopentadienyl Grignard reagent stood in the reaction flask for several months and large colorless needles of $[Cp^{\star}Mg(thf)\mu\text{-}Cl]_2$ grew from the reaction mixture. A single crystal was taken from the flask and several chips were broken off and photographs were taken to determine the best crystal for use in the X-ray diffraction experiment. Even the best crystal diffracted weakly, which, coupled with the presence of a disordered solvent, led to high final R values.

Intensity data were collected on a 0.35 mm × 0.35 mm × 0.50 mm crystal, mounted under nitrogen in a thin-walled glass capillary using a Nicolet R3m/v four-circle diffractometer and Mo-K_α radiation. Cell constants were determined by least-squares methods from the centered angular coordinates of 18 unique intense reflections with 2θ values between 4.85° and 20.32°. During data collection three check reflections were measured every 97 reflections. Atomic scattering factors for H^0, C^0, O^0, Mg^0, and Cl^0 were supplied by Nicolet SHELXTL PLUS (MicroVAX II). Of the 1404 reflections collected, there were 1210 independent reflections (R_{int} = 0.87%), with 843 for which $I > 3.0\sigma(I)$. These data were corrected for absorption based on five psi scans collected at 2θ between 10.76° and 22.81°. The merging R value was lowered from $R = 0.0280$ to $R = 0.0108$ upon application of the absorption correction. Crystal data and refinement parameters are listed in Table 1.

Table 1

Summary of crystal data and data collection parameters for $(Cp^{\star}Mg(thf)\text{-}\mu\text{-}Cl)_2 \cdot \frac{1}{2}C_7H_8$

Formula [a]	$C_{28}H_{46}O_2Cl_2Mg_2$
FW [a], g	533.52
Crystal system	monoclinic
a, Å	21.51(2)
b, Å	11.778(6)
c, Å	14.04(1)
α	90.000°
γ	90.000°
β	95.17(7)°
V, Å^3	3543(5)
Z	4
Density, g/cm^3	1.176
Space group	$C2/c$
Radiation, Å	Mo-K_α = 0.71073
Crystal dimensions, mm	0.35 × 0.35 × 0.50
μ, cm^{-1}	2.4
2θ limits	4°–35°
Total no. of unique data	1210
Unique data used (I > 3σ)	843
Data to parameter ratio	5.1 : 1
Transmission coefficient range	0.670–0.567
R [b]	0.1047
R_w [b]	0.0938
R_G [b]	0.1068
Temperature	−100 °C
Goodness-of-fit	4.86

[a] Excludes solvent molecule. [b] $R = \Sigma(|F_o - F_c|)/\Sigma(F_o)$; $R_w = \Sigma(|F_o - F_c|(W)^{1/2}/\Sigma(F_o(w)^{1/2})$; $R_G = [\Sigma(|F_o - F_c|^2)/\Sigma(F_o)^2]^{1/2}$; $w = 1/\sigma^2(F)$.

Based upon systematic absences, possible space groups were *Cc* and *C*2/*c*. Direct method solutions were attempted in both space groups; solution and refinement in *C*2/*c* produced the most reasonable structure. The initial direct methods solution yielded the chlorine, the magnesium, and the oxygen of the tetrahydrofuran and produced $R = 0.363$. The remaining carbon atoms of the molecule were located from difference maps during several subsequent cycles of least-squares refinement. Fixing the inner carbons of the pentamethylcyclopentadienyl ligand as a rigid group and refining the remaining atoms within $[\mathrm{Cp^{\star}Mg(thf)}\mu\text{-}\mathrm{Cl}]_2$ anisotropically gave an R value of 0.212.

A cluster of atoms of a disordered solvent molecule, which refined as toluene, became evident. The occupancy of these toluene atoms refined to 0.5, which is consistent with the location of the toluene centroid only 0.5 Å from an inversion center. Since the atoms of the phenyl ring refined equally well when treated either independently or as a rigid group, the six-ring atoms were constrained as a rigid group.

In the final refinement the Cp* ring carbons and the toluene ring were refined as rigid groups. The Cp* methyls and the THF atoms, as well as the Mg and Cl were refined anisotropically, while isotropic thermal parameters were refined for the rigid group atoms and the toluene methyl, C(26). Hydrogen atoms were included at fixed

Table 2

Atomic coordinates for $(\mathrm{Cp^{\star}Mg(thf)}\text{-}\mu\text{-}\mathrm{Cl})_2\cdot\frac{1}{2}\mathrm{C_7H_8}$

Atom	x	y	z	U_{iso}
Cl	0.2880(2)	0.3555(4)	0.0660(3)	
Mg	0.3087(2)	0.1576(5)	0.0348(3)	
O(1)	0.3612(5)	0.188(1)	−0.0743(8)	
C(11)	0.370(1)	−0.115(2)	0.016(1)	
C(12)	0.2369(9)	−0.088(2)	0.098(1)	
C(13)	0.2482(9)	0.116(2)	0.246(1)	
C(14)	0.3861(7)	0.217(2)	0.251(1)	
C(15)	0.4595(8)	0.076(2)	0.108(1)	
C(6)	0.3618(8)	0.120(2)	−0.161(1)	
C(7)	0.4046(9)	0.179(2)	−0.220(1)	
C(8)	0.446(1)	0.252(2)	−0.152(2)	
C(9)	0.4035(9)	0.281(2)	−0.080(1)	
C(26)	−0.082(3)	−0.030(5)	0.614(4)	0.15(3)
Rigid groups: Toluene				
C(20)	0.067(1)	0.067(2)	0.485(2)	0.09(2)
C(21)	0.053(1)	0.007(2)	0.400(2)	0.05(1)
C(22)	0.000(1)	−0.062(2)	0.388(2)	0.04(1)
C(23)	−0.039(1)	−0.070(2)	0.462(2)	0.06(1)
C(24)	−0.026(1)	−0.010(2)	0.546(2)	0.05(1)
C(25)	0.027(1)	0.058(2)	0.558(2)	0.07(1)
	Cp*			
C(1)	0.3500(6)	−0.0239(9)	0.0809(7)	0.033(5)
C(2)	0.2921(6)	−0.0130(9)	0.1213(7)	0.041(5)
C(3)	0.2976(6)	0.0777(9)	0.1882(7)	0.029(5)
C(4)	0.3589(6)	0.1229(9)	0.1890(7)	0.032(5)
C(5)	0.3912(6)	0.0602(9)	0.1227(7)	0.038(5)

Table 3

Bond distances and angles for $(Cp^{\star}Mg(thf)\text{-}\mu\text{-}Cl)_2\cdot\frac{1}{2}C_7H_8$

Mg–C(1)	2.38(1)	C(1)–C(11)	1.50(2)
Mg–C(2)	2.39(1)	C(2)–C(12)	1.49(2)
Mg–C(3)	2.38(1)	C(3)–C(13)	1.47(2)
Mg–C(4)	2.37(1)	C(4)–C(14)	1.49(2)
Mg–C(5)	2.37(1)	C(5)–C(15)	1.51(2)
Mg–Cp	2.05	O(1)–C(6)	1.46(2)
Mg–Cl	2.420(7)	C(6)–C(7)	1.47(3)
Mg–Cl(a)	2.412(6)	C(7)–C(8)	1.51(3)
Mg–O(1)	2.02(1)	C(8)–C(9)	1.47(3)
		C(9)–O(1)	1.43(2)
Cl–Mg–O	95.3(4)	Mg–O(1)–C(9)	125.5(1)
Cl–Mg–Cp	122.9(5)	O(1)–C(6)–C(7)	104.9(1)
O(1)–Mg–Cp	120.6(8)	C(6)–C(7)–C(8)	106.3(2)
Cl–Mg–Cl(a)	90.3(2)	C(7)–C(8)–C(9)	101.3(2)
Mg–Cl–Mg(a)	89.7(2)	C(8)–C(9)–O(1)	107.5(2)
Mg–O(1)–C(6)	125.7(1)	C(9)–O(1)–C(6)	108.8(1)

positions for the toluene and THF rings. The methyl hydrogens of the Cp* and the toluene were refined as rigid groups. A group thermal parameter was refined for the Cp* hydrogens, while another group thermal parameter was used for the THF hydrogens. The thermal parameters of the toluene hydrogens were fixed at 0.06 for the ring hydrogens and 0.10 for the methyl hydrogens.

The largest remaining peak on the final difference Fourier map, with an intensity of about 0.5 e/Å^3, is located on the inversion center of the Mg–Cl–Mg–Cl ring. In the last cycle of refinement the largest shift in any parameter, which was for a rotational parameter of the toluene methyl, was 0.9 of its estimated standard deviation. Final atomic coordinates are given in Table 2 and bond distances and angles are summarized in Table 3. Figure 1 is a perspective drawing of the molecule.

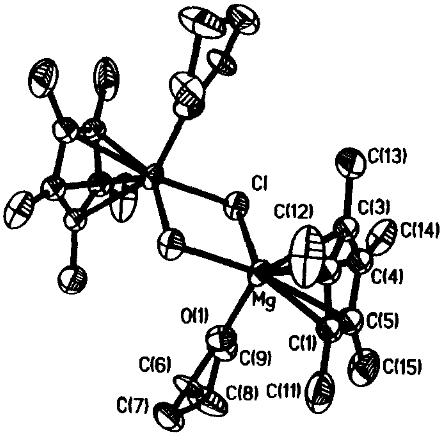

Fig. 1. A labeled perspective drawing of $(Cp^{\star}Mg(thf)\text{-}\mu\text{-}Cl)_2$.

Results and discussion

$[Cp^{\star}Mg(thf)\mu\text{-}Cl]_2$ has crystallographic inversion symmetry about the center of the parallelogram formed by the two magnesiums and the two chlorides. The two magnesium–chlorine distances are essentially the same, 2.420(7) Å and 2.412(6) Å, and fall within the 2.3959(1) to 2.792(9) Å range found in the Mg–Cl–Mg units of $[EtMg_2Cl_3(thf)_3]_2$ [9].

The magnesium is approximately octahedrally coordinated if the pentamethylcyclopentadienyl ring is considered to occupy three sites and the two chloro ligands and the oxygen of the tetrahydrofuran to define the remaining three. In line with this description the Cl–Mg–O(1) angle is 95.3(4)°, the Cl(a)–Mg–O(1) angle is 94.4(4)°, and Cl–Mg–Cl(a) angle is 90.3(2)°. Since the Mg–Cl–Mg(a) angle is 89.7(2)°, the four-membered ring is square within experimental uncertainty. This geometry maximizes distance between both species of the same charge and thus minimizes electrostatic repulsion. The magnesium–oxygen distance, 2.02(1) Å, is slightly shorter than those found in other magnesium THF complexes [12–14], which range from 2.060(1) to 2.11(1) Å.

The five-membered ring of the THF is buckled, which is typical of this molecule [12–14]. Intramolecular steric repulsions within $[Cp^{\star}Mg(thf)\mu\text{-}Cl]_2$ lead to a slight deviation (< 2°) of the methyl groups from the plane of the pentamethylcyclopentadienyl ring, away from the bulk of the molecule.

A significant trend can be found in the average carbon–Mg distances of 2.304(8) Å for Cp_2Mg [15], 2.378(12) Å for $[Cp^{\star}Mg(thf)\mu\text{-}Cl]_2$ (this paper), and 2.417(3) Å for $[CpMg(OEt)]_4$ [12]. In Cp_2Mg, where the Cp–Mg moiety is countered by only a single negative ligand, namely the other cyclopentadienyl, the resulting Mg–C(Cp) bond distance is the shortest. With $[Cp^{\star}Mg(thf)\mu\text{-}Cl]_2$, where the $Cp^{\star}$–Mg moiety is countered by two negatively charged chlorine atoms, intermediate Mg–C(Cp) distances are encountered. Finally, $[CpMg(OEt)]_4$, in which the Cp–Mg moiety is in contact with three negatively charged ethoxy ligands, possesses the longest distance.

Comparing Cp to $Cp^{\star}$, the completely alkylated $Cp^{\star}$ is usually thought to be the better donor. However, in the gas phase the Mg-carbon distances of Cp_2Mg (2.339(4) Å [17]) and $Cp^{\star}_2Mg$ (2.348(9) Å [16]) are indistinguishable, while in the solid state the distance reported here for a $Cp^{\star}$ compound (2.378(12) Å) is both longer [15] than that for the Cp compound Cp_2Mg (2.304(8) Å) and shorter [12] than that of another Cp compound, $[CpMg(OEt)]_4$ (2.417(3) Å). Therefore, there is no structural evidence to indicate that alkylation of Cp groups shortens the Mg–C bonds [18 *].

Supplementary material. Three tables containing supplementary data (Anisotropic Thermal Parameters; Hydrogen Atom Positions; and Observed and Calculated Structure Factors) are available from the authors.

Acknowledgement

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* Reference number with asterisk indicates a note in the list of references.

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18 The average Mg–C bond distance in $[(Me_3Si)_3(C_5H_2)_2Mg$, 2.37(1) Å, which is somewhat longer than those in Cp_2^*Mg and Cp_2Mg, may reflect the steric repulsions between the very bulky $[(Me_3Si)_3(C_5H_2)]$ groups [3]. The average bond distances within $[(Me_3Si)_3(C_5H_2)]Mg(Br)(Me_2NCH_2CH_2NMe_2)$: Mg–C, 2.484(5) Å; Mg–N, 2.264(5) Å and 2.224(5) Å; and Mg–Br, 2.517(3) Å [3], and those in $CpMg(Br)(Me_2NCH_2CH_2NMe_2)$: Mg–C, 2.55 ± 0.05 Å; Mg–N, 2.26 ± 0.09 Å; Mg–Br, 2.63(1) Å [2], appear to be abnormally long when compared to the Mg–C distances discussed in the body of this paper and with normal Mg–Br distances of about 2.45 Å and Mg–N distances of about 2.15 Å [4,5,7]. The reason for the bond lengthening in these molecules is not clear.