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The Preparation of Cyclopentadienyl(neopentyl)-magnesium, its Molecular Structure as Determined by Gas Electron Diffraction, and *ab initio* Molecular Orbital Calculations on Cyclopentadienylmagnesium hydride

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(η^5-C_5H_5)$MgCH_2CMe_3$ (Me=CH_3) and (C_5H_4Me)$MgCH_2CMe_3$ can be prepared by fusion of $Mg(CH_2CMe_3)_2$ and $(C_5H_5)_2Mg$ or $(C_5H_4Me)_2Mg$. The molecular structure of the former has been determined by gas phase electron diffraction. The Mg–C (neopentyl) single bond distance, 212(2) pm, is indistinguishable from that of $Mg(CH_2CMe_3)_2$. The Mg–C(η^5-C_5H_5) bond distance, 232.8(7) pm, is indistinguishable from that in $(C_5H_5)_2Mg$. Self consistent field molecular orbital calculations on (η^5-C_5H_5)MgH with better than DZ basis yield an optimal metal-to-ring distance 2 pm shorter than that obtained by similar calculations on $(C_5H_5)_2Mg$. Metal-to-ring bonding is affected by stabilization of the ring e_1 and a_1 π-orbitals through interactions with Mg $3p_{x,y}$ and *3s* orbitals respectively. The integrated dipole moment is 1.13 D with the negative pole at the apical hydrogen atom.

The gas phase molecular structures of dicyclopentadienyl derivatives of the Group II metals Be, Mg and Zn presents an interesting progression from a half sandwich structure containing one η^5- and one σ-bonded ring, $(C_5Me_5)_2Zn$,[1] through a slip-sandwich structure with one η^5- and one unsymmetrically η^2/η^3 bonded ring, $(C_5H_5)_2Be$,[2] to a symmetric sandwich structure with two η^5-bonded rings; $(C_5H_5)_2Mg$.[3] If the η^5-bonded cyclopentadienyl rings act as 5-electron ligands, the valence shell of the Mg atom in the latter compound accomodates 12 electrons.

The compounds (η^5–$C_5H_4Me)_2Ge$ and (η^5–$C_5Me_5)_2$ Ge have slightly bent sandwich structures in the gas phase,[4,5] in these compounds the valence shell of the metal atom appears to accomodate 14 electrons. There is no doubt that some of these electrons occupy orbitals that are *anti*-bonding between the metal and the ligand ring. In $(C_5Me_5)GeCl$[5], where the number of valence shell electrons of Ge apparently has been reduced by four, the perpendicular metal-to-ring distance has been reduced by 10 pm compared to (η^5–$C_5Me_5)_2Ge$. Moreover, in the ion (η^5–$C_5H_5)Ge^+$ where the metal atom appears to be

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surrounded by an electron octet, the optimal metal-to-ring distance obtained by high-quality *ab initio* calculations, is shorter still by 12 pm.[6]

It occurred to us, therefore, that the mean Mg–C(Cp) bond distance in a cyclopentadienyl-magnesium-alkyl, where the Mg atom presumably is surrounded by an octet of electrons, might be significantly shorter than in the 12-electron species $(C_5H_5)_2Mg$. We first tested this hypothesis by carrying out *ab initio* MO calculations on the model compound $(\eta^5-C_5H_5)MgH$ and comparing the optimal Mg-ring distance with that obtained by similar calculations on $(\eta^5-C_5H_5)Mg$.[7] The calculations indicated that the difference was very small, of the order of 2 pm. We nevertheless decided to test the assumption by carrying out a structure determination of a suitable compound.

Variable temperature ^1H NMR have shown that $(C_5H_5)_2Mg$ and $(CH_3)_2Mg$ in ether solvents redistribute to the unsymmetrical species, $(C_5H_5)MgCH_3$:[8]

$$Cp_2Mg + Me_2Mg \rightleftarrows 2\ CpMgMe$$

with K=18.8 and $\Delta G°=-7.2$ kJ in tetrahydrofuran at 25 °C.[9] $CpMgMe(OEt_2)$ has, however, been reported to disproportionate on removal of the diethylether at room temperature.[10] The driving force of this reaction is presumably the formation of solid, polymeric $(Me_2Mg)_x$.

Since $(Me_3CCH_2)_2Mg$ is volatile[11] and monomeric in the gas phase,[12] as is Cp_2Mg,[2] we thought that the unsymmetrical species, $CpMgCH_2CME_3$, should be stable with respect to disproportionation and exist as a monomer in the gas phase.

Cyclopentadienyl-neopentylmagnesium was prepared by melting together equimolar amounts of Cp_2Mg and $(Me_3CCH_2)_2Mg$ at 120 °C, followed by crystallization from toluene. The methylcyclopentadienyl complex $(MeC_5H_4)(Me_3CCH_2)Mg$ was prepared similarly. Both complexes are volatile and give molecular ions in the mass spectrometer. Full preparative and spectroscopic details are given in the experimental section.

EXPERIMENTAL

Synthesis. All operations were carried out under nitrogen. Analyses were performed by the microanalytical laboratory at the University of California, Berkeley. The NMR spectra were recorded on a JEOL FX-90Q instrument operating at 89.56 MHz for proton and 22.50 MHz for carbon at 26 °C in deuterated benzene and the chemical shifts are expressed in δ-units relative to tetramethylsilane. Electron Ionization mass spectra were recorded on a AEI–MS–12 machine equipped with a direct inlet.

$CpMgCH_2CMe_3$. Dicyclopentadienylmagnesium[13] (2.6 g, 0.017 mol.) and dineopentylmagnesium[11] (2.8 g, 0.017 mol.) were melted together at 120 °C under nitrogen. The melt was stirred for 8 hours, then cooled to room temperature. The white solid was crystallized as colourless plates from toluene, *ca.* 10 ml, −10 °C. Yield was 4.6 g, 76 %, m.p. 139–142 °C. The complex sublimed at 70–80 °C/10^{-2} mm. *Anal.* Calculated for $C_{10}H_{16}Mg$: C, 74.9; H, 9.98. Found: C, 75.0; H, 10.0. M^+; 160. NMR ^1H, δ 6.03 s (5H) C_5H_5; 1.06 s (9H) Me_3C; −0.04 s (2H) CH_2. $^{13}C\{^1H\}$, δ 107.2, C_5H_5; 36.6, Me_3C; 28.2, Me_3C; 31.6, CH_2.

$(MeC_5H_4)MgCH_2CMe_3$. Di(methylcyclopentadienyl)-magnesium prepared by replacing C_5H_6 by Me C_5H_5 in Ref. 13[14] (2.6 g, 0.015 mol) and dineopentylmagnesium (2.5 g, 0.015 mol) were melted together at 100 °C. The melt was stirred for 2 hours, then cooled to room temperature. Pentane (*ca.* 10 ml) was added to the liquid yielding a white solid. Pentane was removed under reduced pressure and the solid residue was sublimed at 40–50 °C/10^{-2} mm as colorless prisms, m.p. 70–72 °C. Yield was 4.5 g (87 %). *Anal.* Calculated for $C_{11}H_{18}Mg$: C, 75.7; H, 10.3. Found: C, 75.9; H 10.0. M^+=174. NMR: ^1H; The AA'BB' protons of the MeC_5H_4-ring appear as a multiplet centered at δ 6.0 (4H); δ 2.09 s (3H) MeC_5H_4; 1.15 s

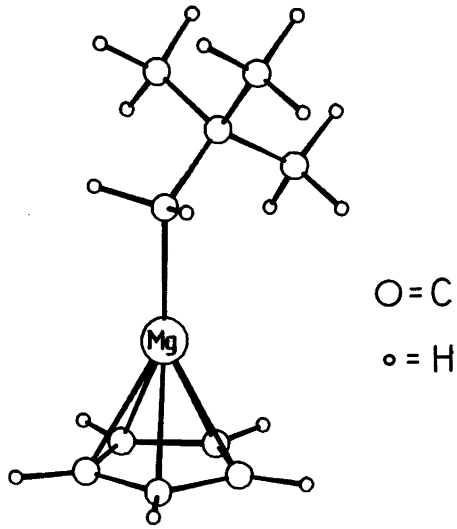

Fig. 1. Molecular model of $(\eta^5-C_5H_5)Mg\ CH_2CMe_3$.

(9H) Me_3C; 0.03 s (2H) CH_2. ^{13}C; The cyclopentadienyl carbon atoms appear at δ 119.6, s; 107.1, d, JCH=170 HZ; 105.6, d, JCH=170 Hz; 36.6, q, JCH=124 Hz, Me_3C; 29.0, s. Me_3C; 31.8, t, JCH=97 Hz, CH_2; 13.9, q. JCH=127 Hz, ring Me.

Gas electron diffraction. The GED patterns of $CpMgCH_2CMe_3$ were recorded on Balzers Eldigraph KDG-2 with nozzle and reservoir temperatures of about 90 °C, corresponding to a vapor pressure of about 1 torr. Exposures were made with nozzle-to-plate distances of 50 and 25 cm. Five plates of each set were photometered and the optical densities processed by standard procedures. The molecular intensity curves for each nozzle-to-plate distance were averaged but not connected. The curves extended from s=20 to 137.5 nm^{-1} with increment Δs=1.25 nm^{-1} (50 cm) and from s=45 to 250 nm^{-1} with increment Δs=2.50 nm^{-1}.

The complex atomic scattering factors, $f'(s)$, were calculated from an analytical representation of the atomic potential,[15] using a program written by Yates.[16] The molecular intensities were modified by multiplication with $s/|f_c||f_{Mg}|$.

CALCULATIONS

Structure refinements. A molecular model of $CpMgCH_2CMe_3$ is shown in Fig. 1. Initial refinements were based on a model of C_s symmetry constructed in the following way:

(i) The (C_5H_5) ring was assumed to have D_{5h} and the $(C_5H_5)Mg$ fragment to have C_{5v} symmetry as in $(C_5H_5)_2Mg$.

(ii) The neopentyl-Mg fragment was constructed from a neopentane molecule of T_d symmetry by removing a H atom and replacing it with Mg. The ∠MgCC valence angle was allowed to vary, while the plane of the methylene group was assumed to bisect ∠MgCC. The ∠HCH angle of the methylene group was fixed at 109.5°. The valence angle ∠CCH(Me) was fixed at 112.4°, the value found in $Mg(CH_2CMe_3)_2$.[12]

(iii) The $Mg-C_\alpha$ σ-bond was assumed to coincide with the C_5 symmetry axis of the $(C_5H_5)Mg$ fragment. The relative orientation of the two ligands were fixed as indicated in Fig. 1, yielding a model with a symmetry plane .

The molecular model constructed in this manner is described by seven independent parameters, *e.g.* the three bond distances of the $(C_5H_5)Mg$ fragment; Mg–C, C–C and C–H, the three bond distances of the Mg-neopentyl fragment, and the valence angle ∠MgCC.

These parameters were refined by least-squares calculations on the intensity data with a diagonal weight matrix. Five r.m.s. amplitudes of vibration, *l*, were included in the refinement. Non refined amplitudes were fixed at values found in Cp_2Mg[2] and $Mg(CH_2CMe_3)_2$.[12] Vibrational corrections (shrinkage) were neglected. These refinements led to satisfactory agreement between experimental and calculated scattering intensities, and between experimental and between calculated radial distribution curves, except around r=450 pm, where we find the *anti* (τ=180°) Mg···C distance of the Mg-neopentyl fragment.

It does not seem unreasonable to assume that the neopentyl group undergoes large amplitude libration about the $C_\alpha-C_\beta$ bond. The list of independent parameters was therefore augmented by a thermal average value for the dihedral angles τ(MgCCC), and the refinement repeated. The best values for the structure parameters are listed in Table 1. The estimated standard deviations have been multiplied by a factor of three to compensate for additional uncertainties introduced by data correlation and simplifying assumptions built into the model.

Experimental and calculated radial distribution curves are compared in Fig. 2. We consider the agreement very satisfactory.

Molecular orbital calculations. Ab initio MO calculations were carried out using the program DISCO[17] with Gaussian type basis. For calculations on the compound $(C_5H_5)MgH$ we used a (12, 9, 2) basis contracted to <7, 5, 2> on Mg[18], a (9, 5, 1) basis contracted to <4, 2, 1> on C[19], and a (3) basis contracted to <2> on H[20]. Calculations on $(C_5H_5)_2Mg$ by Faegri and coworkers show that this basis set yields an optimal perpendicular metal-to-ring distance (h) only 2.3 pm greater than the experimental value.[7]

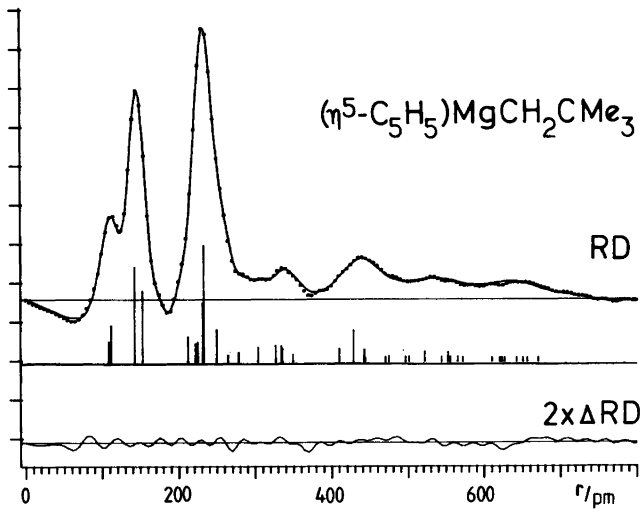

Fig. 2. Experimental radial distribution (RD) curve for $(\eta^5-C_5H_5)Mg\ CH_2CMe_3$. Full line; theoretical RD curve calculated for best model. Major interatomic distances are indicated by vertical bars of height approximately proportional to the area under the corresponding peak. Below: Difference curve. Artificial damping constant k=20 pm^2.

The C_5H_5 ring was assumed to have D_{5h} symmetry with bond distances C–C=142 pm and C–H=112 pm. The Mg–H and Mg–ring distances were optimized by carrying out calculations on nine different combinations of values for Mg–H and h. The optimal values were Mg–H=171 pm and h=201 pm.

RESULTS AND DISCUSSION

In Table 1 we compare the structure parameters of $(C_5H_5)MgCH_2CMe_3$ (I) with the parameters obtained by similar GED studies of $(C_5H_5)_2Mg$ (II)[2] and $Mg(CH_2CMe_3)_2$ (III).[12]

The Mg–C_α single bond distances and vibrational amplitudes (l) in I and III are indistinguishable. So are the Mg–C(Cp) bond distances in I and II. The r.m.s. Mg–C(Cp) vibrational amplitudes indicate that the bonding is stiffer in I, but the difference hovers at the edge of statistical significance. Moreover, the Mg–Cp stretching force constants obtained by *ab initio* calculations on CpMgH and Cp_2Mg are very similar, 1.94 and 1.86 mdyn/Å respectively.

The optimal Mg–H bond distance in CpMgH, 171 pm, is close to the experimental bond distance in diatomic MgH, 173 pm.[21] The perpendicular Mg-to-ring distance, h=201 pm, is 2 shorter than the optimal distance in Cp_2Mg calculated with the same basis,[7] and differs from the experimental value in I by only 3 pm. Thus, experiment and calculations both indicate that h is only slightly – if at all – increased on going from I to II.

The highest occupied molecular orbitals of CpMgH are described and their energies compared to those of the Cp-radical[7] in Table 2. The Mg–to–ring bonding seems to be affected to about the same degree by stabilization of the e_1 and a_1 π-orbitals through interactions with the Mg $3p_{x,y}$ and $3s$ orbitals, respectively. Atomic and overlap populations are listed in Table 3. As pointed out by Faegri and coworkers[7] population analysis give little information on charge distribution when – as in the present case – the atomic basis is larger than double zeta.

Table 1. Bond distances, valence angles and r.m.s. vibrational amplitudes of $(\eta^5-C_5H_5)Mg$ CH_2CMe_3. Estimated standard deviations in parentheses in units of the last digit.

	r_a(pm)	l(pm)	r_a(pm)	l(pm)
$Mg(\eta^5-C_5H_5)$ fragment			$Mg(C_5H_5)_2$[c]	
Mg–C	232.8(7)	8.3(7)	233.9(4)	10.3(3)
C–C	142.6(4)	4.6(7)[a]	142.3(2)	4.4(1)
C–H	108.8(6)	10.3(6)[b]	111.6(7)	7.8(7)
h	198.7(7)		200.8(4)[d]	
Mg-neopentyl fragment			$Mg(CH_2CMe_3)_2$[e]	
Mg–C	212(2)	8.3(20)	212.6(6)	8.6(5)
C–C	153.2(5)	5.9(7)[a]	154.1(2)	5.9(2)
C–H	111.9(6)	10.3(6)[b]	110.5(2)	7.2(2)
∠MgCC (°)	126(4)		118.3(12)	
∠CCC (°)	(109.5)		(109.5)	
∠CCH (°)	(112.4)		112.4(7)	
τ(Mg CCC) (°)	41(10)		(0)	

[a] Refined with constant difference. [b] Assumed equal. [c] Ref. 3. [d] Corrected for shrinkage. [e] Ref. 12.

Table 2. Highest occupied orbitals of CpMgH and the Cp radical.

CpMgH		ε(ev)	Cp ε(ev)[a]
5 e_1	Cpπ+Mg $p_{x,y}$	−8.97	− 8.16
8 a_1	H *s*+Mg *s*	−10.34	
3 e_2	Cpσ	−14.39	−14.32
7 a_1	Cpπ+Mg *s*	−15.02	−13.22

[a] Ref. 7.

Table 3. Atomic and overlap populations for (C_5H_5)Mg H.

Mg *s*	4.66
px, py	2.13
pz	2.35
dz^2	0.22
d (other)	0.05
total	11.54
H (apical)	1.04
(C_5H_5)	35.42
Mg−H	0.41
Mg−Cp	0.32

The intergrated dipole moment is 1.13 Debye with the negative pole at the apical hydrogen atom. The relatively modest dipole moment does not necessarily imply that charge separation in the molecule is negligible. In this context it may be pertinent to recall that the dipole moment of the diatomic molecule LiH is 6.0 D.[21] Li is only slightly more electropositive than Mg and the metal-H bond distance (160 pm)[21] only slightly shorter than in CpMgH. We believe therefore that the small dipole moment in CpMgH is due to canceling of large, opposite Mg−Cp and Mg−H bond polarities.

Why is the metal-to-ring distance in $(C_5H_5)MgCH_2CMe_3$ indistinguishable from that in $(C_5H_5)_2Mg$? Clearly it is not sufficient to count the number of excess (*i.e.* beyond the octet) electrons nominally in the valence shell of the metal atom: In $(C_5H_5)_2Mg$ the four excess electrons occupy *ligand centered* e_1'' π orbitals that do not appear to interact with metal orbitals.[7] In $(C_5H_5)_2Ge$ and in $(C_5H_5)GeCl$, two of the excess electrons occupy *metal centered* (lone pair) orbitals with strong *antibonding* interactions with the Cp ligand.[4]

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