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Structure and spectra of methylmagnesium Grignard complexes

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The results of *ab initio* quantum chemistry calculations at the HF/6-31G* and MP2/6-31G* levels for the structure and vibrational spectra of the CH_3MgX and CH_3MgMgX (X = F, Cl, Br) Grignard reagents are presented.

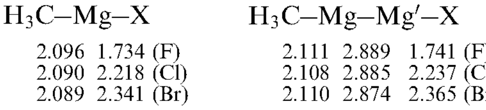
Low temperature matrix reactions of the alkyl halides CH_3X (X = Cl, Br) with magnesium atoms and clusters have been suggested to result in intriguing bi-magnesium species of the type CH_3MgMgX along with the conventional Grignard reagents CH_3MgX.[1–5] The subject gained increased attention due to indirect indications of a higher reactivity of magnesium clusters compared to single metal atoms.[1–3] However, there is no direct experimental evidence of formation of bi-magnesium Grignard reagents and no detailed theoretical investigations proving that metal clusters Mg_n ($n > 1$) are reactive species under matrix isolation conditions.

The motivation for the present theoretical study is twofold. First, by performing quantum chemistry simulations of IR spectra for a variety of possible products of the reactions of CH_3X with magnesium atoms or clusters we provide a guideline for spectral experimental identification of Grignard reagents. Cryogenic syntheses of such substances are almost complete and studies of the reactions of CH_3X (X = Cl, Br) + Mg_n ($n = 1, 2, ...$) will be carried out, in particular with vibrational spectroscopy techniques.

Second, when comparing quantum chemistry results for the series of Grignard complexes CH_3MgX and CH_3MgMgX (X = F, Cl, Br) obtained in this and in previous[5] studies a remarkable picture of bonding in these substances arises which requires special discussion.

All calculations have been carried out at the *ab initio* Hartree–Fock (HF) and second-order Møller–Plesset perturbation theory (MP2) levels with the GAMESS program suite.[6] The unrestricted version (UHF) has been employed for open shell species. The conventional 6-31G* basis sets have been used for all atoms except Br for which the Billing–Curtiss DZV(d) set has been applied as prescribed by the GAMESS strategy.[6]

The HF/6-31G* optimized equilibrium geometries for the Grignard reagents $H_3C{-}Mg{-}X$ and $H_3C{-}Mg{-}Mg'{-}X$ (all of them possess the C_{3v} symmetry) are shown in Figure 1. These results are consistent with all previous *ab initio* calculations.[4,5,7–9] In particular, the HF results of Davis[9] for the $H_3C{-}Mg{-}F$ and $H_3C{-}Mg{-}Cl$ species differ from our values by less than 0.02 Å. If electron correlation effects are taken into account the calculated geometry parameters differ (insignificantly for our purposes) from those given in Figure 1. For instance, for the fluorine species[5] an inclusion of correlation contributions leads to an elongation of the Mg–F distances by 0.04 Å and a shortening of the Mg–Mg distance by 0.03 Å. The same conclusion may be drawn from the results of Davis[9] for $H_3C{-}Mg{-}F$ and $H_3C{-}Mg{-}Cl$ species when comparing the HF and MP2 geometries: the differences fall



$H_3C{-}Mg{-}X$		$H_3C{-}Mg{-}Mg'{-}X$		
2.096	1.734 (F)	2.111	2.889	1.741 (F)
2.090	2.218 (Cl)	2.108	2.885	2.237 (Cl)
2.089	2.341 (Br)	2.110	2.874	2.365 (Br)

Figure 1 Equilibrium geometry configurations (the HF/6-31G* results). Shown are the C–Mg, Mg–Mg′ and Mg–X distances (in Å).

Table 1 Binding energies in kcal mol^{-1} for the Grignard species computed at the MP2/6-31G*//HF/6-31G* level.

Channel	F	Cl	Br
CH_3–Mg–X → CH_3X + Mg	56.2	52.4	57.9
CH_3–Mg–Mg–X → CH_3–Mg–X + Mg	6.7	6.2	8.2
CH_3–Mg–Mg–X → CH_3X + Mg_2	62.8	58.5	66.0
CH_3–Mg–Mg–X → CH_3Mg + MgX	42.2	42.1	45.3

within 0.03 Å.

Binding energies of the Grignard reagents with respect to various dissociation channels (RMgX → RX + Mg; RMgMgX → RMgX + Mg; RMgMgX → RX + Mg_2; RMgMgX → RMg + MgX), computed using the MP2 theory (for HF/6-31G* optimized geometries), are collected in Table 1. The results obtained previously[5] for the fluorine species are included for completeness. Clearly, all these compounds are stable systems towards possible decompositions. The formation of bi-magnesium Grignard reagents is energetically justified since energy gains are noticeable (6–8 kcal mol^{-1}) when passing from RMgX to RMgMgX species. It should be noted that the binding energies behave non-monotonically in the series F, Cl, Br.

Tables 2 and 3 give the computed harmonic frequencies and relative IR intensities for MgX, RX, RMgX, RMgMg′X (R = CH_3; X = Cl, Br) species calculated at the HF/6-31G* level. The results for the fluorine species may be found in ref. 5. The frequencies are scaled with a conventional scaling factor 0.9. The accuracy of such a procedure may be estimated by comparing theoretical values with the known experimental results.[10–12]

Table 2 Harmonic frequencies (cm^{-1}, scaling factor 0.9) and relative IR intensities (in parentheses) calculated at the HF/6-31G* level for the RMgMg′Cl, RMgCl, RCl and MgCl species (R = CH_3). Experimental frequencies are shown after the solidus.

RMgMg′Cl	RMgCl	RCl	MgCl
57 (0.5)			
116 (0)	112 (1.0)		
169 (0.1)			
431 (3.0)	338 (0.4)		412 (2.1)/465 [13]
513 (0.5)	575 (2.2)		
533 (0.7)	580 (2.4)	700 (1.1)/733 [12]	
		1020 (0.1)/1017 [12]	
1173 (0.1)	1176 (0)	1372 (0.6)/1355 [12]	
1424 (0)	1424 (0)	1451 (0.1)/1452 [12]	
2804 (1.8)	2823 (0.8)	2899 (0.8)/2968 [12]	
2866 (1.0)	2891 (0.6)	2996 (0.2)	

It is thus possible to distinguish bi-magnesium Grignard reagents from the corresponding mono-magnesium species by their IR spectra. The main difficulty may be masking of the bands originating from the reaction products of primary interest (CH_3MgX and CH_3MgMgX) by the bands from MgX, MgX_2, CH_3X, C_2H_6, *etc.* If, however, this problem is solved the frequency differences between CH_3MgX and CH_3MgMgX are noticeable enough to be detected spectroscopically.

Table 3 Harmonic frequencies (cm^{-1}, scaling factor 0.9) and relative IR intensities (in parentheses) calculated at the HF/6-31G* level for the RMgMg′Br, RMgBr, RBr and MgBr species (R = CH_3). Experimental frequencies are shown after the solidus.

RMgMg′Br	RMgBr	RBr	MgBr
65 (0.3)			
139 (0)	123 (0.8)		
148 (0.1)			
383 (2.1)	280 (0.4)		345 (1.6)/374 [13]
512 (0.7)	562 (2.2)		
533 (0.7)	578 (2.2)	582 (0.6)/610 [12]	
		955 (0.1)/955 [12]	
1173 (0.1)	1177 (0)	1327 (1.0)/1305 [12]	
1426 (0)	1428 (0)	1447 (0.1)/1443 [12]	
2803 (1.8)	2822 (0.9)	3010 (0.7)/3057 [12]	
2866 (1.0)	2890 (0.7)	3012 (0.1)	

The electronic structure of mono- and bi-magnesium Grignard reagents is also interesting. First of all we note that, according to the natural bond orbital (NBO) analysis,[13] for all mono-magnesium species the Lewis structures with a carbon–magnesium bond are predicted, *i.e.* $\mathrm{R{-}Mg}\,:\!\ddot{\underset{\cdot\cdot}{\mathrm{X}}}\!:$, and for all bi-magnesium compounds, the Lewis structures with metal–metal bond are preferable, $\mathrm{R{:}Mg{-}Mg'}\!:\!\ddot{\underset{\cdot\cdot}{\mathrm{X}}}\!:$. This is consistent with both the partial charges on atoms (see Table 4) and the effective electronic configurations of constituent atoms. We show explicitly the results of population analysis for the bromine species since for other halogens the results are similar:

CH_3MgBr:
$C(2s^{1.28}2p^{4.09})$ $H(1s^{0.77})$ $Mg(3s^{0.42})$ $Br(4s^{1.97}4p^{5.82})$

$CH_3MgMg'Br$:
$C(2s^{1.29}2p^{4.13})$ $H(1s^{0.78})$ $Mg(3s^{0.99})$ $Mg'(3s^{1.09})$ $Br(4s^{1.97}4p^{5.86})$

The only noticeable changes when passing from mono- to bi-magnesium molecules involves occupation of the 3*s* orbitals on Mg. In bi-metallic species the electronic configuration of both magnesium atoms is [core] $3s^1$ and the formation of metal–metal bond Mg–Mg′ is explicable.

According to the population analysis (natural charges on atoms are given in Table 4), insertion of either one or two magnesium atoms into the C–X bonds results in highly ionic substances. For the monomagnesium Grignard reagents the oxidation state of Mg is intermediate between +1 and +2 (charges are within 1.5–1.6 units). Insertion of two metal atoms causes almost the same distortions in charge distributions in the local arrangements as in the case of one atom, and the total charge of both magnesium atoms, Mg and Mg′, in $CH_3MgMg'X$ is close to the charge on Mg in CH_3MgX, while the oxidation state of Mg and Mg′ is +1.

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Table 4 Natural charges on atoms (HF/6-31G* calculations) for the RX, RMgX and RMgMg′X species (R = CH_3).

Atom	RMgMg′F	RMgF	RF	RMgMg′Cl	RMgCl	RCl	RMgMg′Br	RMgBr	RBr
C	−1.468	−1.427	−0.096	−1.465	−1.408	−0.610	−1.464	−1.407	−0.688
H	0.218	0.226	0.175	0.220	0.229	0.237	0.219	0.229	0.244
Mg	0.876	1.640		0.918	1.566		0.920	1.527	
Mg′	0.855			0.779			0.739		
X	−0.917	−0.892	−0.429	−0.891	−0.846	−0.101	−0.852	−0.806	−0.043

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