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Structure of Magnesium Cluster Grignard Reagents

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Structures of the magnesium Grignard complexes CH_3MgF, CH_3MgMgF, $CH_3MgF(Mg)$, and $CH_3MgF(Mg_2)$ have been studied by *ab initio* methods of quantum chemistry, including self-consistent-field, many-body perturbation theory, and density functional theory techniques. Electronic distributions have been analyzed by means of natural bond orbital analysis. It has been found that magnesium atoms can be attached to the Grignard reagent CH_3MgF, leading to a dimagnesium complex $CH_3MgF(Mg)$ and the trimagnesium species $CH_3MgF(Mg_2)$. The energy of the $CH_3MgF(Mg)$ complex is found to be lower than that of the previously known CH_3MgMgF compound.

Introduction

During the last several years there has been a notable increase in research on the structure of the Grignard reagents that occur in the reactions of alkyl halides with magnesium atoms and clusters.[1−9] It has been suggested[2,3] that magnesium clusters Mg_n may be more active in reactions with CH_3Hal than single magnesium atoms, leading to the formation of CH_3−Mg−Mg−Hal species via multicenter transition states. Inspired primarily by experimental findings,[1−4] a series of quantum chemical calculations have been described in the literature[5−9] for the Grignard reagents CH_3MgX and CH_3MgMgX (X = F, Cl). The structure of CH_3MgF has been studied computationally by Baskin et al.[5] Sakai and Jordan[6] have computed the equilibrium geometry and vibrational frequencies of CH_3MgCl and compared their results with those of IR investigations of matrix-isolated species by Ault.[4] Jasien and Dykstra[7,8] have shown that cluster reagents CH_3−Mg−Mg−X, as well as single-atom magnesium compounds CH_3MgX, are thermodynamically stable species and that their occurrence in low-temperature reactions, as studied by Klabunde et al.[1−3] under matrix-isolation conditions, may be expected. Davis[9] has computed vibrational frequencies, geometries, and transition state energies for the insertion reactions Mg + CH_3F → CH_3MgF and Mg + CH_3Cl → CH_3MgCl and discussed the potential energy surfaces for these reactions. Despite the cited theoretical and experimental studies, and a recent review article,[10] the role of magnesium clusters in reactions and in formation of complicated Grignard reagents still remains to be explored, especially questions about multimagnesium reactions.

In the present study we show that the regular Grignard molecule CH_3−Mg−F can accommodate extra magnesium atoms, leading to interesting intermolecular complexes: $CH_3MgF(Mg)$, which is strongly bound and possesses an even lower energy than the previously studied double-magnesium Grignard reagent CH_3−Mg−Mg−F, and $CH_3MgF(Mg_2)$. Our conclusions are based on the results of *ab initio* calculations with the help of the conventional MO LCAO and density functional theory (DFT) approaches. We employ natural bond orbital (NBO) analysis[11,12] to elucidate details of electronic structures of all the species involved. Natural bond orbital analysis has proven its usefulness for studying many systems, in particular those that are primarily ionic in nature,[13] as is the case of Grignard reagents. We then relate the results of our calculations to those previously reported for the stable hypermagnesium oxides Mg_nO (*n* = 2−4).[14]

Geometries and Energies

Calculations have been performed using the GAMESS,[15] GAUSSIAN 92,[16] and DGauss[17] software packages. In the

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calculations using the conventional Hartree–Fock (HF) and second-order Moller–Plesset (MP2) routines, standard 6-31G* basis sets have been utilized. For those calculations carried out using density functional techniques, we employed the nonlocal spin density (NLSD) formalism with the Becke exchange[18] and the Lee–Yang–Parr correlation[19] potentials within the DZVP basis set[20] representation. We made this particular choice of the DFT approach for the following reasons. It is well-known that *ab initio* calculations of molecular constants for the ground state of Mg_2 have problems due to difficulties in providing a proper description of correlation effects and that considerable efforts are required to properly describe the Mg–Mg bond.[23,24] We have found that the NLSD(LYP)/DZVP approach gives reasonable values of $R_e = 3.92$ Å, $\omega_e = 56.5$ cm^{-1}, and $D_e = 345.5$ cm^{-1} for Mg_2 (which can be compared to the experimental properties $R_e = 3.89$ Å, $\omega_e = 51.1$ cm^{-1} and $D_e = 430$ cm^{-1}). These NLSD(LYP) results are considerably better than those obtained in our preliminary and previous[25] calculations using other DFT approximations, such as LSD or NLSD with different (Becke–Perdew[25]) exchange-correlation potential. In addition, we have found that this choice of the DFT approach has been successful in characterizing the small conformational energy differences among conformers of different compounds.[21,22] Since correlation effects are expected to play a significant role in the bonding between the Mg atoms, and since we expect small energy differences between some of the Grignard complexes, our experience led us to choose this particular DFT description.

Optimized structures for all species were calculated at the HF/6-31G* and NLSD/DZVP levels. Because correlation is not expected to play an important role in the determination of geometries, Moller–Plesset perturbation theory was not included in geometry optimizations. It was used only for energy calculations at the HF-optimized geometries. Figure 1 shows the molecular arrangements for the following systems: CH_3F molecule (**I**) CH_3–Mg radical (**II**), regular Grignard reagent CH_3–Mg–F (**III**) double-magnesium CH_3–Mg–Mg radical (**IV**), double-magnesium Grignard reagent CH3–Mg–Mg-F (**V**), double-magnesium complex $CH_3MgF(Mg)$ (**VI**), triple-magnesium complex $CH_3MgF(Mg_2)$ (**VII**), transition state $[CH_3MgF]$ (**VIII**) for the insertion reaction $CH_3F + Mg \rightarrow CH_3{-}Mg{-}F$. The energies presented in Tables 1 and 2 have been obtained at the MP2/6-31G*//HF/6-31G* and NLSD(LYP)/DZVP levels. Table 1 lists the total energies of the systems, and Table 2 gives the binding energies of the Grignard compounds relative to the decomposition products.

These data confirm that both single-magnesium CH_3–Mg–F (**III**) and double-magnesium CH_3–Mg–Mg-F (**V**) Grignard reagents are stable species. However, another double-magnesium complex (**VI**), designated here as $CH_3MgF(Mg)$, has been found with an energy which is even lower than that of the previously known CH_3–Mg–Mg–F compound. Along with its unexpected geometry configuration, the electronic structure of $CH_3MgF(Mg)$ is also very peculiar as will be discussed below. The triple-magnesium species **VII**, $CH_3MgF(Mg_2)$, is also a bound system with a binding energy of about 2 kcal/mol with respect to $CH_3MgF(Mg)$ + Mg. This is typical for weak intermolecular complexes, but the complex exhibits unusually short intermolecular distances. Both approaches used here, MP2//HF and NLSD, give results consistent with each other; however, it should be pointed out that the binding energies of all stable species are found to be somewhat lower in the NLSD approximation.

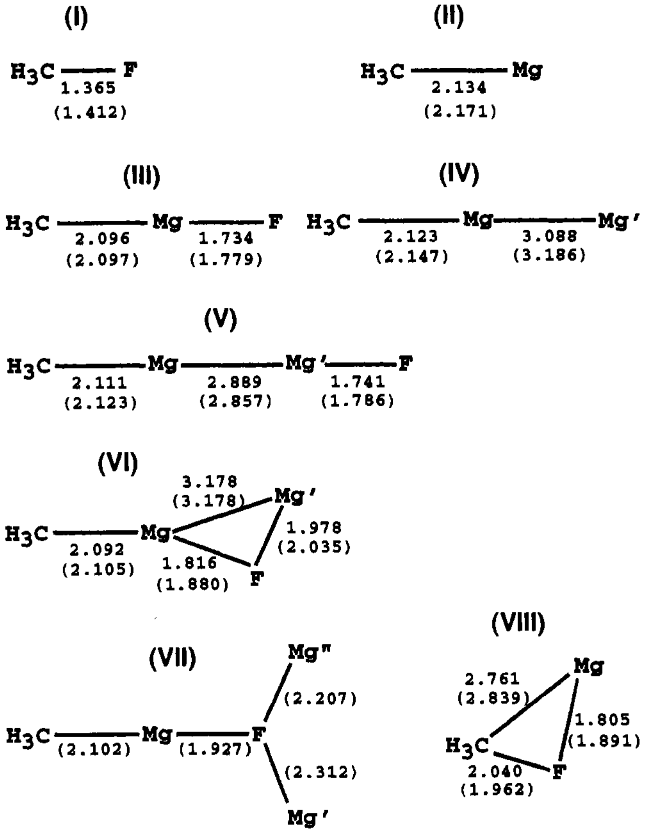

Figure 1. Geometry configurations of the studied Grignard complexes and related species. Bond lengths (in Å), calculated at the HF/6-31G* and NLSD/DZVP (in parentheses) levels, are indicated. Geometry parameters for the CH_3 group are not shown; for instance, in the CH_3F molecule $R_{CH} = 1.083$ (1.104) Å and ∠HCF = 109° (109°). Species **I**–**V** possess C_{3v} symmetry; **VI** and **VIII** C_s symmetry. Angular parameters for structure **VI** are as follows: ∠HCMg = 112° (111°), ∠CMgMg = 163° (163°), ∠MgFMg = 114° (108°), ∠MgMgF = 35° (38°). For structure **VII**: ∠HCMg = (111°), ∠CMgF = (170°), ∠Mg'FMg = (109°), ∠Mg"FMg = (99°), ∠Mg'FMg" = (151°). For structure **VIII**: ∠HCMg = 83° (76°), ∠CMgF = 48° (44°).

Table 1. Total Energies (au)[a]

struct no.	species	MP2/6-31G*// HF/6-31G*	NLSD(LYP)/ DZVP
	Mg	−199.617 597	−200.053 196
	Mg_2	−399.235 342	−400.107 966
	MgF	−299.277 299	−299.957 634
	CH_3	−39.692 699	−39.817 711
I	CH_3F	−139.359 557	−139.745 341
II	CH_3Mg	−239.350 468	−239.908 055
III	CH_3MgF	−339.066 636	−339.873 771
IV	CH_3MgMg	−438.978 372	−439.969 941
V	CH_3MgMgF	−538.694 940	−539.932 948
VI	$CH_3MgF(Mg)$	−538.706 719	−539.944 358
VII	$CH_3MgF(Mg_2)$		−740.000 218
VIII	$[MgCH_3F]$	−338.933 943	−339.768 429

[a] Structure numbering according to Figure 1.

Table 3 shows the unscaled harmonic frequencies of the stable molecules **I**–**VI** calculated with the HF/6-31G* approach. Molecule **VII** was found to be unstable by the HF/6-31G* calculations; therefore the frequencies for structure **VII**

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Table 2. Binding Energies (Activation Energies in the Case of **VIII**, [CH_3MgF]) in kcal/mol for the Grignard Species[a]

channel		MP2	NLSD
III	$CH_3{-}Mg{-}F \rightarrow CH_3F + Mg$	56.2	47.2
V	$CH_3{-}Mg{-}Mg{-}F \rightarrow CH_3{-}Mg{-}F + Mg$	6.7	3.8
	$CH_3{-}Mg{-}Mg{-}F \rightarrow CH_3F + Mg_2$	62.8	50.0
	$CH_3{-}Mg{-}Mg{-}F \rightarrow CH_3Mg + MgF$	42.2	42.2
VI	$CH_3MgF(Mg) \rightarrow CH_3{-}Mg{-}F + Mg$	14.1	10.9
	$CH_3MgF(Mg) \rightarrow CH_3{-}Mg{-}Mg{-}F$	7.4	7.2
VII	$CH_3MgF(Mg_2) \rightarrow CH_3MgF(Mg) + Mg$		1.7
VIII	$[CH_3MgF] \leftarrow CH_3F + Mg$	27.1	18.9

[a] MP2 means MP2/6-31G*//HF/6-31G* values; NLSD stands for NLSD(LYP)/DZVP energies.

($CH_3MgF(Mg_2)$)) are shown as calculated by the DFT. Regularities in the series reflect common structural features easily recognized for these substances. Of particular interest is a position of the line originating from the Mg−F vibration near 780 cm^{-1}. This frequency is characteristic for possible identifications of the species which may be presented among the products of the Mg + CH_3F reaction. From this point of view the structural fragment Mg−F is obviously present in the CH_3−Mg−Mg−F species. It may be also recognized in CH_3−Mg−F and $CH_3MgF(Mg)$. However, frequency shifts from the pure Mg−F value are considerable, indicating certain perturbations in the structures. It should be noted that for all these compounds the lines approximately assigned to a Mg−F vibration are IR active with noticeable intensities.

NBO Description

A picture of the Lewis structures of substances **I**−**VIII** arising from the NBO analysis is presented in Figure 2 (a canonical pattern for the CH_3 fragment is not shown explicitly). Table 4 gives the natural partial charges on atoms for these systems.

Obviously all these substances (with an exception of CH_3F) are highly ionic species. The charge polarization is easily seen when one follows the electronic distribution in the course of Mg insertion into the C−F bond via the transition complex [CH_3MgF].

Stability of the double-magnesium Grignard reagent CH_3−Mg−Mg−F (**V**) may be related to formation of the structural unit (Mg−Mg) with a total partial charge +1.7—the diatomic cation Mg_2^+ is known to be considerably more stable than the neutral molecule Mg_2. Peculiarly, some of the local properties of single- and double-magnesium Grignard reagents CH_3−Mg−F (**III**) and CH_3−Mg−Mg−F (**V**) are similar. Distances from carbon and fluorine to the closest magnesium atoms are as follows: R(C−Mg) = 2.10 Å in **III** and 2.11 Å in **V**; R(Mg−F) = 1.73 Å in **III** and 1.74 Å in **V**. Partial charges on atoms in **III** and **V** are also similar (a total charge of the Mg−Mg unit in **V** is +1.73 versus a charge of +1.64 for the single Mg atom in **III**. It seems as though an insertion of the dimagnesium species into the C−F bond leads to the same changes in the local arrangements as that of a single Mg atom.

The reasons for stability of the lowest energy double-magnesium species $CH_3MgF(Mg)$ (**VI**) are less obvious than those for CH_3−Mg−Mg−F (**V**). From the NBO analysis we can conclude that species **VI** may be described as an intermolecular complex of the regular Grignard reagent CH_3−Mg−F with the Mg atom. It should be noted that there is one more stationary point (not discussed here in detail) on the potential energy surface of CH_3MgF + Mg which may be viewed as the weakly bound molecular adduct CH_3MgF••Mg in the entrance channel of the reaction CH_3MgF + Mg. However, although the formal Lewis diagrams and charge distributions of structure **VI** are practically the same as those for a molecular adduct, $CH_3MgF(Mg)$ (**VI**) differs considerably by geometry (notice short internuclear distances from fluorine to both magnesium atoms in **VI** and binding energy toward decomposition CH_3MgF + Mg (i.e. more than 10 kcal/mol for **VI** and less than 1 kcal/mol for an adduct) from such a complex CH_3−Mg−F••Mg.

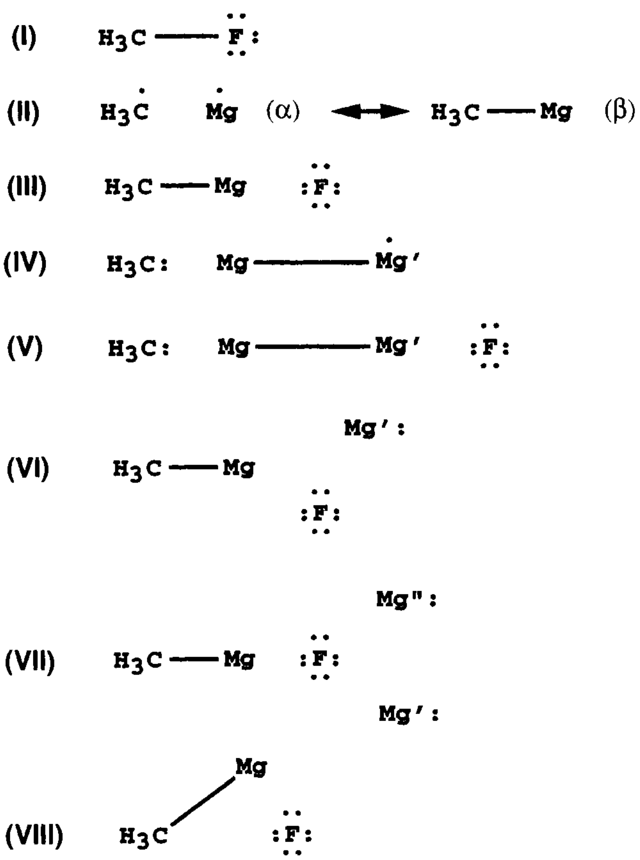

Figure 2. Natural bond orbital description (Lewis structures) of species **I**−**VIII**. Canonical pattern for the CH_3 group is omitted to simplify the representation. For the CH_3Mg molecule (**II**) the NBO analysis was performed separately for the systems of electrons with α and β spins.

An instructive way to explain stability of intermolecular complexes within the NBO picture is to dinstinguish particular delocalization effects accompanying complex formation.[11] In the case of the $CH_3MgF(Mg')$ (**VI**) species, the NBO analysis shows that important effects arise from the partial transfer of electron density from the lone pair orbital (n) of the Mg′ atom to both antibonding orbital σ^*(C−Mg) and fluorine Rydberg orbital (Ry(F)). As NBO analysis showed, the particular stabilization energy contributions related to the n(Mg′) → σ^*(C−Mg) and n(Mg′) → Ry(F) charge transfers[11] amount to 10 and 13 kcal/mol, respectively. These effects are negligible on the NBO structure of the adduct CH_3−Mg−F••Mg.

The double-magnesium Grignard complex $CH_3MgF(Mg)$ can hold one more magnesium atom, resulting in structure **VII**, shown in Figure 1, which according to the NBO analysis may be described as an intermolecular complex of the CH_3−Mg−F molecule with two Mg atoms. As we mentioned before, correlation effects play a critical role in describing multimagnesium species; in particular, we have not located the stationary point **VII**, $CH_3MgF(Mg_2)$, with the Hartree−Fock method, and the analysis has been performed with the NLSD data.

It is interesting to compare the hypermagnesium Grignard complexes with the hypermagnesium oxides.[14] According to ref 14 the natural charges on magnesium atoms in oxides are considerably lower (less than +1.0) than those for the species

Table 3. Harmonic Frequencies (cm^{-1}) Calculated at the HF/6-31G* Level (for $CH_3MgF(Mg_2)$ (**VII**) at the NLSD/DZPV Level)

CH_3MgFMg_2 (**VII**)	CH_3MgFMg (**VI**)	CH_3MgMgF (**V**)	CH_3MgF (**III**)	CH_3MgMg (**IV**)	CH_3Mg (**II**)	CH_3F (**I**)	CH_3	MgF
36								
51								
58								
73	73	69		72				
89	78	69		72				
99	97	130	136					
130	110	130	136					
168		209		172				
370	362						340	
598	458	563	488	541	511			
601	622	578	634	562	565			
602	627	578	634	562	565			
	700	782	836					779
						1186		
1149	1294	1298	1300	1290	1259	1307		
						1307		
1435	1580	1582	1583	1581	1580	1633	1529	
1436	1582	1582	1583	1581	1580	1633	1530	
2951	3166	3132	3153	3109	3121	3203	3236	
3034	3239	3199	3227	3180	3199	3286	3417	
3037	3243	3199	3227	3180	3199	3286	3420	

Table 4. Natural Charges on Atoms (HF/6-31G* Calculations) for the Stable Species and for the Transition State $[CH_3MgF]$

atom	CH_3MgFMg_2 (**VII**)	$CH_3MgF(Mg)$ (**VI**)	CH_3MgMgF (**V**)	CH_3MgMg (**IV**)	CH_3Mg (**II**)	CH_3MgF (**III**)	$[CH_3MgF]$ (**VIII**)	CH_3F (**I**)
C	−1.430	−1.425	−1.468	−1.464	−1.423	−1.427	−0.236	−0.096
H	0.232	0.228	0.218	0.216	0.219	0.226	0.228	0.175
H	0.231	0.228	0.218	0.216	0.219	0.226	0.233	0.175
H	0.231	0.230	0.218	0.216	0.219	0.226	0.238	0.175
Mg	1.612	1.608	0.876	0.757	0.767	1.640	0.344	
Mg′	0.027	0.064	0.855	−0.058				
F	−0.931	−0.934	−0.917			−0.892	−0.807	−0.429
Mg″	0.028							

studied here. One of the structures for Mg_3O denoted (C_{2v}, I)[14] possesses the charge distribution close to that of the Grignard complexes $CH_3MgF(Mg)$ and $CH_3MgF(Mg_2)$; namely, one of the magnesium atoms holds zero charge but is bound to the Mg_2O fragment at a distance typical for a normal chemical bond.

Conclusions

As we mentioned in Introduction, it has been suggested[2,3] that formation of multimagnesium Grignard reagents by a direct insertion of Mg_n into the C−Hal bond might occur under some experimental conditions. This idea gained support from the thermodynamic stability of $CH_3{-}Mg{-}Mg{-}X$ established computationally. However, at present, there are neither direct experimental evidences of such a process nor theoretical confirmations which should include locations of the corresponding transition states. Clearly an attempt to find a reaction pathway, e.g. for the $Mg_2 + CH_3X \rightarrow CH_3{-}Mg{-}Mg{-}X$ reaction, will be unsuccessful since the dimagnesium molecule should dissociate if the energy is increased by an amount much less than the expected potential barrier for insertion. More likely, formation of multimagnesium Grignard complexes may occur upon subsequent addition of the magnesium atoms to the regular Grignard reagent $CH_3{-}Mg{-}X$. Taking into account results of the present study, such an addition in the case of fluorine reactions should occur via formations of the intermolecular complexes

$$CH_3{-}Mg{-}F + Mg \rightarrow CH_3MgF(Mg)$$

$$CH_3MgF(Mg) + Mg \rightarrow CH_3MgF(Mg_2)$$

but not via insertions into the chemical bonds.

According to the NBO analysis, the methylmagnesium Grignard species are highly ionic substances, which is typical for many hypermetal compounds.[26] Formation of the C−Mg bond is a special feature of these systems. If, however, two magnesium atoms are involved in the bonding ($CH_3{-}Mg{-}Mg$, $CH_3{-}Mg{-}Mg{-}F$), then a metal−metal bond should be considered. From this point of view, a lower energy of the double-magnesium complex $CH_3MgF(Mg)$ compared to $CH_3{-}Mg{-}Mg{-}F$ signifies that the C−Mg bond is stronger than Mg−Mg.

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