1,10-Phenanthroline and Its Complexes with Magnesium Compounds. Disproportionation Equilibria

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The solvation, complexation, and disproportionation equilibria, which might be important during titration of a Grignard reagent RMgX with an alcohol in the presence of 1,10-phenanthroline (phen), have been studied both in the gas phase and solution using the density functional theory (DFT) B3LYP/6-31+G* method. Solvation was modeled using the supermolecule approach. NBO atomic charge analyses were performed at the B3LYP/6-31G* level. The absorption spectra of the complexes were calculated by the DFT TD/MPW1PW91/6-311+G** method. According to our calculations the complexation of magnesium halide MgX_2 with 1,10-phenanthroline is the reason for the disappearance of the red color of the complex RMgX(phen) near the titration end point.

1. Introduction

Grignard reagents RMgX (X = halogen) have been known for more than hundred years[1] and have found widespread applications in organic synthesis.[2,3] One of the simplest methods for determination of a Grignard reagent concentration is the titration of its solution with *s*-butanol[4] in the presence of 1,10-phenanthroline (**phen**) as an indicator. This method yields the Grignard reagent concentration with ordinary volumetric precision.

Phen is thought to form simple reversibly coordinated 1:1 charge transfer (CT) complexes[4] with organomagnesium compounds such as RMgX and R_2Mg.[5,6] There is, however, some controversy about the color of a Grignard reagent complex with **phen** in the literature. So, Lindsell[2] mentions the violet-green color of the complex, while other works[5,7] indicate that the complex should be red or burgundy. Our experimental work[8] also evidenced that the complex between a Grignard reagent and **phen** has deep red color. The measured absorption spectrum[8] of the complex C_2H_5MgBr(phen) had intense absorption maxima at 522, 440, and 392 nm corresponding to the n-π^* excitations in the CT complex, and at 316 nm corresponding to a $\pi-\pi^*$ transition in the π-system of **phen**. However, it is known that R_2Mg also forms colored complexes with **phen**.[4−6]

To the best of our knowledge, no information is available regarding the processes which take place during titration of a Grignard reagent with an alcohol in the presence of **phen** and the reasons for the disappearance of the color of the solution near the titration end point. It can be assumed that an alkoxymagnesium halide which forms during the titration reaction

$$\mathrm{RMgX} + \mathrm{R^1OH} \rightarrow \mathrm{R^1OMgX} + \mathrm{RH} \qquad (1)$$

either does not form the complex with **phen** or the complex is colorless.

It should be also remembered that in solution Grignard reagents do not have a simple constitution but exist as an equilibrium mixture which may involve various solvated components. The primary equilibrium, known generally as the Schlenk equilibrium,[9] is the dismutation process, expressed simply by eq 2:

$$2\mathrm{RMgX} \rightleftharpoons \mathrm{R_2Mg} + \mathrm{MgX_2} \qquad (2)$$

It is well-known that the Schlenk equilibrium depends on the solvent[2,3] but the dependence on the concentration of the solution is still unclear. As a rule the Schlenk equilibrium is shifted toward the formation of RMgX in diethyl ether.[2,3] In the case of THF the equilibrium is more shifted toward the formation of R_2Mg and MgX_2 because of better solvation of the magnesium halide.[2,3]

Similar equilibrium reactions can take place in case of alkoxymagnesium halide (i.e., the product of titration reaction):

$$2\mathrm{ROMgX} \rightleftharpoons \mathrm{(RO)_2Mg} + \mathrm{MgX_2} \qquad (3)$$

As a result, the constitution of the titration mixture at the titration end point is not evident.

A number of theoretical studies on the structures, energies, atomic charges, mechanism of formation reaction, and other properties of Grignard reagents have been carried out using different ab initio calculations based on the Hartree−Fock (HF) method, the Møller−Plesset (MP) perturbation theory, the coupled cluster (CC) method, etc., and also the density functional theory (DFT).[10−19] To our knowledge the disproportionation equilibria of Grignard reagents have been investigated only by semiempirical calculations using the extended Hückel MO[20] and CNDO/2[21] methods.

In the current work we investigated the solvation, complexation, and disproportionation equilibria, which might take place during titration of a Grignard reagent with an alcohol in the presence of **phen**, by means of DFT calculations. The influence of solvent on these above-mentioned equilibria was also modeled. We also calculated (by TD-DFT method) the absorption spectra of all possible complexes of **phen** to clarify the

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reasons for the disappearance of the red color of the solution near the titration end point.

2. Calculation Methods

All calculations were carried out using the GAUSSIAN 98[22] program package.

We investigated the disproportionation equilibria (the Schlenk equilibria) according to eqs 2 and 3 ($R = CH_3$, and $X = Cl$, Br) and complexation equilibria of all formed species with **phen**.

Optimizations and vibrational analysis were done using the density functional theory (DFT) with hybrid B3LYP functional and the 6-31+G* basis set. All stationary points were found to be true minima (number of imaginary frequencies, NImag = 0). The calculated frequencies were also used for calculations of enthalpies and Gibbs free energies. The stability of the complexes of **phen** was calculated considering the basis set superposition error (BSSE) estimated according to the counterpoise correction method of Boys and Bernardi.[23]

Solvation was modeled using the supermolecule approach. Up to two molecules of dimethyl ether were added to the studied species. The basis set superposition error was taken into account here too. The BSSE had a particularly strong influence on both the complexation and solvation energies of the bromine containing compounds compared to the corresponding chlorine compounds.

Also, the natural bond orbital (NBO)[24] analysis was performed for all the investigated species at the B3LYP/6-31G* level.

The absorption spectra of **phen** and its complexes with the studied magnesium compounds were calculated by the time-dependent density functional theory (TD-DFT) using hybrid MPW1PW91 density functional with the 6-311+G** basis set. The DFT TD/MPW1PW91/6-311+G** method has been found to give excitation energies in satisfactory agreement with experiment.[25]

3. Results and Dicussion

3.1. Calculated Absorption Spectra for Complexes of 1,10-Phenanthroline with CH_3MgCl, CH_3OMgCl and Corresponding Disproportionation Products. Calculated absorption spectra are given in Figure 1. Corresponding excitation energies and oscillator strengths are given in Table 1. The measured absorption spectrum of **phen**[8] (in CH_3CN) had some weak bands at 330, 322, and 308 nm, a band of medium intensity in the region 274−286 nm, the two most intense bands at 262 and 230 nm with a shoulder, and a band of medium intensity at 196 nm. Comparison of experimental[8] and calculated spectra of **phen** (Table 1) indicates that the calculated excitation energies are shifted to shorter wavelengths (hypsochromic shift). Despite the fact that the calculated spectrum of CH_3MgCl(phen) complex (Table 1) does not have a good correlation with the experimentally measured absorption spectrum[8] of C_2H_5MgBr(phen) complex (see Introduction), the calculations still clearly predict the absorption in the visible region. The absorption of light by the complex $(CH_3)_2Mg$(phen) (Table 1) also occurs in the visible region according to our calculations, in a good agreement with experimental data.[5,6] No information was found in the literature regarding the absorption spectrum of the $(RO)_2Mg$(phen) complex.

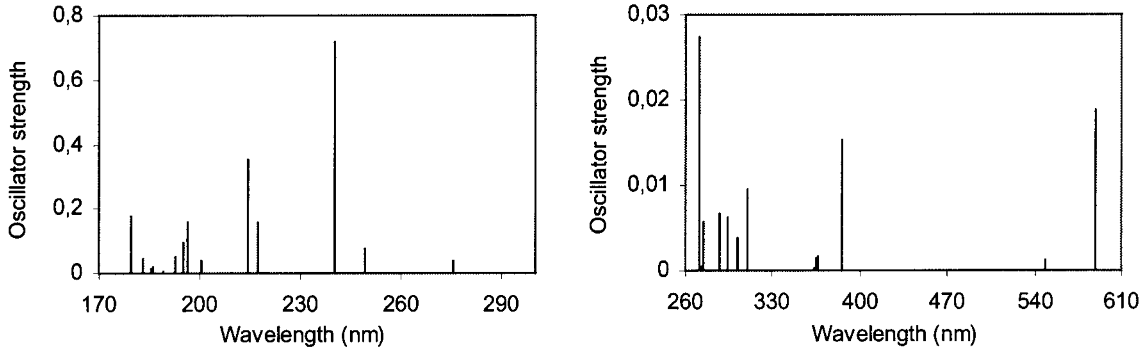
So, our results indicate that all complexes of **phen** with alkyl- and alkoxymagnesium compounds have intense absorption maxima in the visible region (Figure 1b−e). Thus, the disappearance of the color at the equivalence point of titration of a Grignard reagent with an alcohol in the presence of **phen** cannot be attributed to the formation of the complex between ROMgX and **phen** as the complex should be also colored according to our calculations.

TABLE 1: Calculated Excitation Energies (nm) and Oscillator Strengths for 1,10-Phenanthroline and Its Complexes with Magnesium Compounds at DFT TD/MPW1PW91/6-311+G Level of Theory**

	nm	osc. strengths
1,10-phenanthroline	275	0.0396
	248	0.0768
	240	0.7192
	217	0.1567
	214	0.3510
	196	0.1557
	195	0.0930
	192	0.0519
	179	0.1735
CH_3MgCl(phen)	588	0.0187
	386	0.0153
	309	0.0095
	301	0.0039
	294	0.0062
	286	0.0066
	273	0.0057
	271	0.0275
CH_3OMgCl(phen)	562	0.0041
	374	0.0103
	308	0.0071
	296	0.0029
	294	0.0093
	291	0.0082
	290	0.0042
$(CH_3)_2Mg$(phen)	743	0.0558
	736	0.0042
	519	0.0172
	439	0.0052
	349	0.0044
	318	0.0193
	289	0.0500
	287	0.0172
	273	0.0218
$(CH_3O)_2Mg$(phen)	606	0.0096
	529	0.0025
	369	0.0028
	305	0.0047
	302	0.0065
$MgCl_2$(phen)	378	0.0120
	361	0.0045
	312	0.0162
	297	0.0089
	294	0.0116
	278	0.0043
	268	0.0076

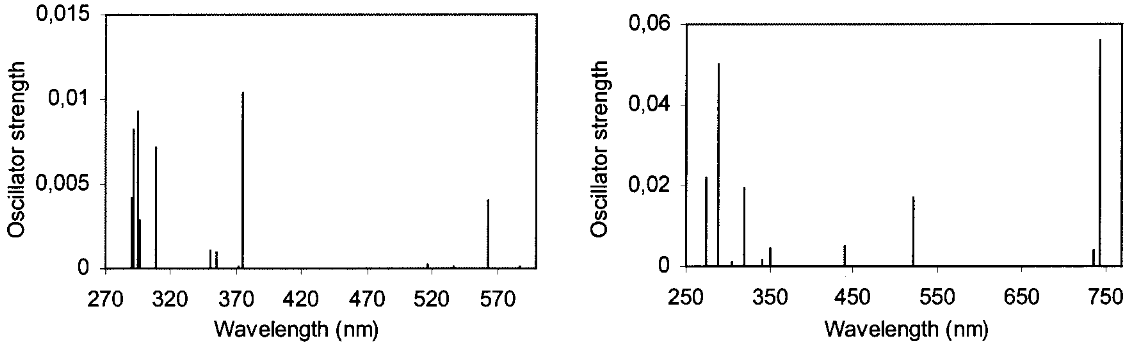
The complex of **phen** with magnesium halide (Figure 1f) is the only one without absorption in the visible region. This leads to the necessity to investigate the Schlenk equilibrium (eq 2) as an alkoxy complex which forms during titration of a Grignard reagent with an alcohol can disproportionate according to the Schlenk equilibrium (eq 3).

3.2. Solvation Equilibria. The calculated solvation energies of studied species with one or two dimethyl ether molecules are given in Table 2. The geometries of mono- and disolvated species are shown in Figures 2 and 3. The tricoordinated magnesium is planar in the monosolvated complexes while the tetracoordinated magnesium forms with its ligands a deformed tetrahedron in the disolvated complexes, in accordance with the cristallographic data.[26] The solvation reaction is exothermic for all the studied species. The chlorine compounds are somewhat more strongly solvated than the corresponding bromine componds. The solvation energies (with both one and two solvent



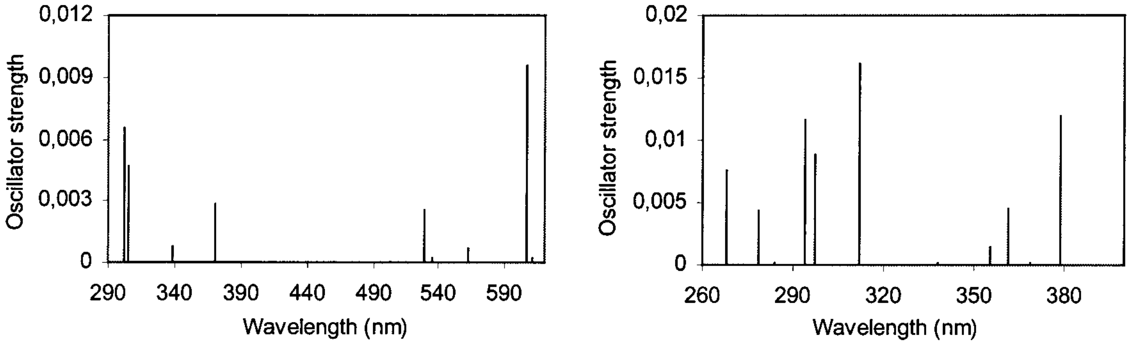
a) 1,10-phenanthroline

b) CH_3MgCl(phen)



c) CH_3OMgCl(phen)

d) $(CH_3)_2Mg$(phen)



e) $(CH_3O)_2Mg$(phen)

f) $MgCl_2$(phen)

Figure 1. Calculated (at TD/MPW1PW91/6-311+G** level of theory) absorption spectra of (a) 1,10-phenanthroline, (b) CH_3MgCl(phen), (c) CH_3OMgCl(phen), (d) $(CH_3)_2Mg$(phen), (e) $(CH_3O)_2Mg$(phen), and (f) $MgCl_2$(phen).

TABLE 2: The Solvation Energies (ΔE, contains zero-point vibrational energy (ZPVE) correction), Enthalpies (ΔH), and Gibbs Free Energies (ΔG) of Magnesium Compounds with One or Two Dimethyl Ether Molecules at B3LYP/6-31+G* Level (All values are given in kcal/mol and are corrected for basis set superposition error (BSSE).)

	$Z + n(CH_3)_2O \rightarrow Z{\cdot}n(CH_3)_2O$					
	ΔE		ΔH		ΔG	
Z	$n = 1$	$n = 2$	$n = 1$	$n = 2$	$n = 1$	$n = 2$
$MgCl_2$	−23.0	−39.3	−23.0	−39.1	−13.8	−20.1
$MgBr_2$	−19.2	−34.1	−19.3	−33.8	−9.7	−13.8
CH_3MgCl	−16.7	−28.4	−16.5	−27.9	−6.9	−8.2
CH_3MgBr	−14.8	−25.8	−14.6	−25.3	−5.2	−5.5
CH_3OMgCl	−21.4	−36.4	−21.4	−35.9	−11.3	−15.6
CH_3OMgBr	−20.1	−34.4	−20.0	−33.9	−9.8	−13.6
$(CH_3)_2Mg$	−11.7	−19.5	−11.1	−18.5	−3.2	−0.4
$(CH_3O)_2Mg$	−20.2	−33.4	−20.2	−33.0	−10.6	−12.9

TABLE 3: The Complexation Energies (ΔE, contains zero-point vibrational energy (ZPVE) correction), Enthalpies (ΔH), and Gibbs Free Energies (ΔG) at B3LYP/6-31+G* Level (All values are given in kcal/mol and are corrected for basis set superposition error (BSSE).)

	$Z + \text{phen} \rightarrow Z(\text{phen})$		
Z	ΔE	ΔH	ΔG
$MgCl_2$	−43.9	−43.9	−33.6
$MgBr_2$	−39.9	−39.8	−29.3
CH_3MgCl	−33.0	−32.6	−22.9
CH_3MgBr	−31.8	−31.2	−21.9
CH_3OMgCl	−38.6	−38.4	−28.6
CH_3OMgBr	−36.9	−36.6	−26.1
$(CH_3)_2Mg$	−24.5	−23.7	−15.2
$(CH_3O)_2Mg$	−34.0	−33.7	−23.7

molecules) are higher for magnesium halides ($\Delta H_1 = -23.0...-19.3$ and $\Delta H_2 = -39.1...-33.8$ kcal/mol, respectively) and methoxy compounds ($\Delta H_1 = -21.4...-20.0$ and $\Delta H_2 = -35.9...-33.0$ kcal/mol, respectively). This can evidently be related to a lesser steric hindrance to the interaction between the magnesium atom and the oxygen atom(s) of the solvent.

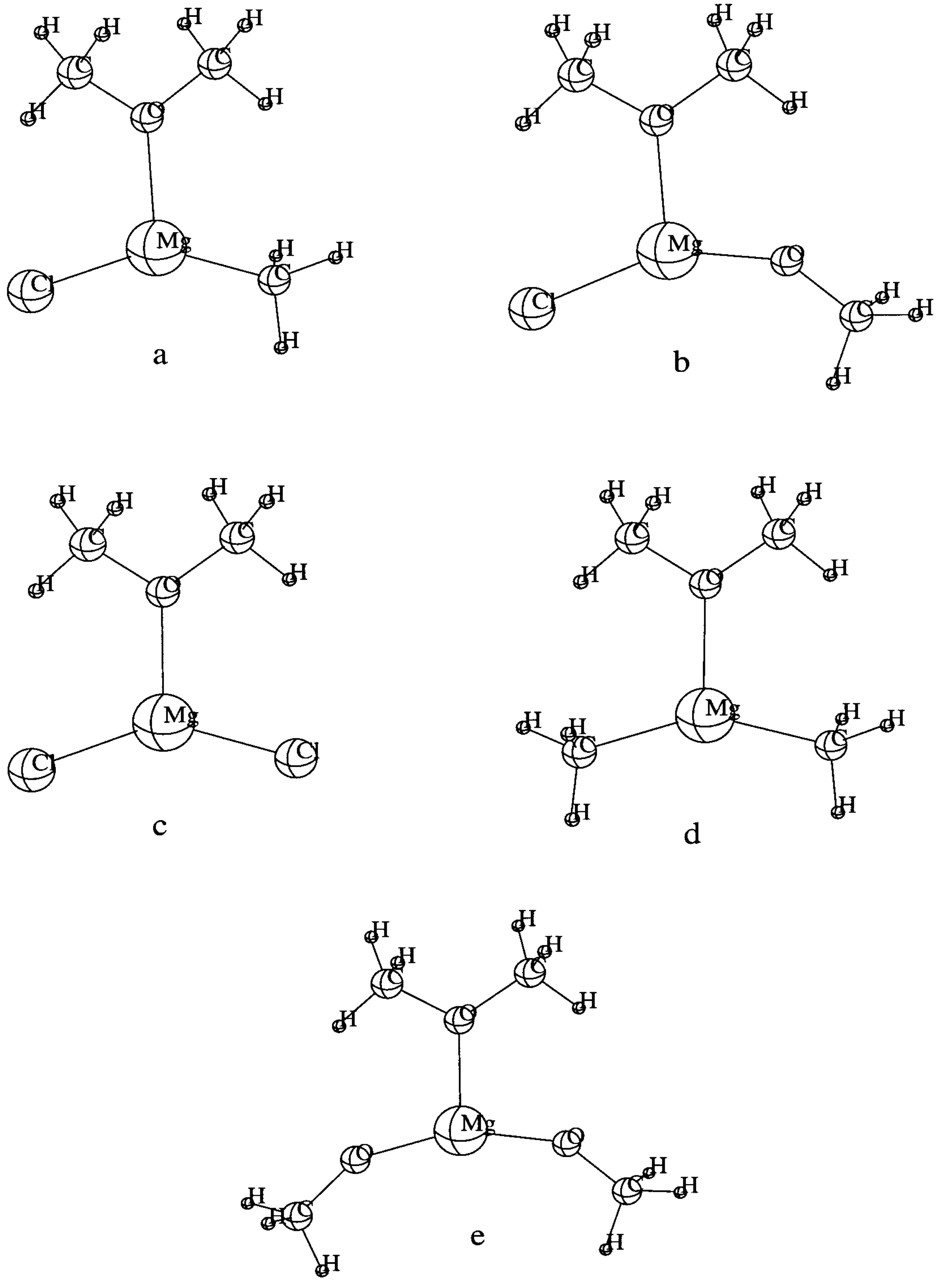


Figure 2. The optimized (at B3LYP/6-31+G* level of theory) structures of monosolvated (a) CH_3MgCl, (b) CH_3OMgCl, (c) $MgCl_2$, (d) $(CH_3)_2Mg$, and (e) $(CH_3O)_2Mg$.

The distances between the magnesium atom and the oxygen atom(s) of the solvent are 2.050−2.059 Å in the monosolvated and 2.094−2.099 Å in the disolvated magnesium halides, and 2.043−2.049 Å in the monosolvated and 2.095−2.097 Å in the disolvated methoxy compounds. Another possible reason (besides steric consideration) for higher solvation energies of magnesium halides and methoxy compounds is the higher positive charge on the metal atom in these species. The atomic (NBO) charge on magnesium is the highest in $(CH_3O)_2Mg$ for all cases (+1.727 in the unsolvated, +1.702 in the monosolvated, and +1.716 in the disolvated compound). The atomic charges on magnesium are somewhat greater in the chlorine compounds compared to the corresponding bromine compounds (see Table 5). In accordance with a hypothesis that the solvation energy is determined by the charge on magnesium atom and the steric hindrance to the interaction of the solvent and metal atom (the bulkiness of ligands), the solvation energy is the lowest ($\Delta H_1 = -11.1$ and $\Delta H_2 = -18.5$ kcal/mol, respectively) in case of $(CH_3)_2Mg$ which is sterically the most crowded with two relatively bulky methyl groups directly bound to the magnesium atom, and has the smallest atomic charge on magnesium (+1.370 in the unsolvated, +1.454 in the mono-

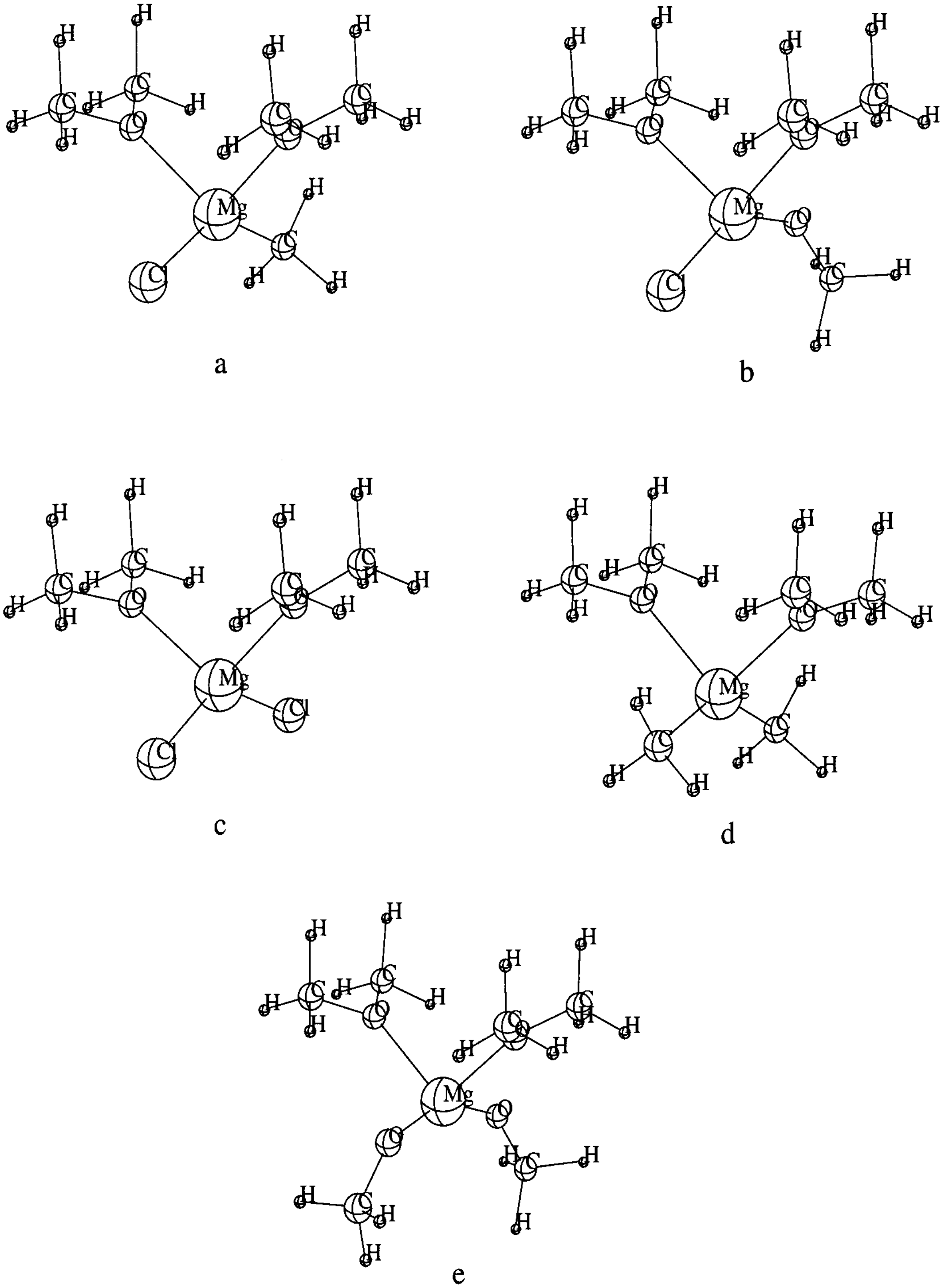


Figure 3. The optimized (at B3LYP/6-31+G* level of theory) structures of disolvated (a) CH_3MgCl, (b) CH_3OMgCl, (c) $MgCl_2$, (d) $(CH_3)_2Mg$, and (e) $(CH_3O)_2Mg$.

solvated, +1.517 in the disolvated compound, see Table 5). The distances between the magnesium atom and the oxygen atom(s) of the solvent is 2.147 Å in the monosolvated and 2.196 Å in the disolvated compound. The solvation energies with both one and two solvent molecules and the above-mentioned bond lengths stay between the two extremes in case of methylmagnesium halides ($\Delta H_1 = -16.5...-14.6$ kcal/mol, $r_1 = 2.097-2.105$ Å, and $\Delta H_2 = -27.9...-25.3$ kcal/mol, $r_2 = 2.137-2.145$ Å, respectively).

3.3. The Complexation Energies. The complexation energies of studied molecules (unsolvated, mono-, and disolvated) with **phen** were calculated from eq 4 where Z = MgX_2, CH_3MgX, CH_3OMgX, $(CH_3)_2Mg$, and $(CH_3O)_2Mg$, and the number of solvent molecule(s) $n = 0$, 1, and 2.

$$Z{\cdot}n(CH_3)_2O + \text{phen} \rightleftharpoons Z(\text{phen}) + n(CH_3)_2O \qquad (4)$$

The results are given in Tables 3 and 4. For the unsolvated (gas-phase) species the complexes of **phen** with magnesium halides are the most stable ($\Delta H = -43.9...-39.8$ kcal/mol). This is apparently due to the fact that two electronegative halogen atoms withdraw larger amount of the electron density

TABLE 4: The Complexation Energies (Δ*E*, contains zero-point vibrational energy (ZPVE) correction), Enthalpies (Δ*H*), and Gibbs Free Energies (Δ*G*) of Mono- and Disolvated Species at B3LYP/6-31+G* Level (All values are given in kcal/mol and are corrected for basis set superposition error (BSSE).)

	$Z{\cdot}n(CH_3)_2O + \text{phen} \rightarrow Z(\text{phen}) + n(CH_3)_2O$					
	Δ*E*		Δ*H*		Δ*G*	
Z	*n* = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2
$MgCl_2$	−20.8	−4.5	−20.8	−4.8	−19.8	−13.5
$MgBr_2$	−20.7	−5.8	−20.5	−6.0	−19.6	−15.4
CH_3MgCl	−16.3	−4.6	−16.1	−4.7	−16.0	−14.7
CH_3MgBr	−17.0	−6.0	−16.6	−5.9	−16.7	−16.4
CH_3OMgCl	−17.2	−2.2	−17.1	−2.5	−17.4	−13.1
CH_3OMgBr	−16.7	−2.5	−16.6	−2.7	−16.3	−12.5
$(CH_3)_2Mg$	−12.9	−5.1	−12.7	−5.2	−12.0	−14.8
$(CH_3O)_2Mg$	−13.8	−0.6	−13.6	−0.7	−13.1	−10.8

from magnesium thus allowing stronger electrostatic interaction between the more positively charged magnesium and the negatively charged nitrogens of **phen**. The complexation energy is the lowest in case of the complex of **phen** with $(CH_3)_2Mg$ ($\Delta H = -23.7$ kcal/mol) which is sterically the most unfavorable and has the smallest positive charge on magnesium (+1.490).

The solvation of the magnesium compounds causes a remarkable decrease in the complexation energies as one of the reagents (magnesium compound) is stabilized by the specific solvation while the product (complex) is not solvated. The complexation energies of **phen** with disolvated $MgCl_2$, CH_3MgCl, and $(CH_3)_2Mg$ are very close ($\Delta H = -5.2...-4.7$ kcal/mol). The complexes of **phen** with $MgBr_2$ and CH_3MgBr have also close stabilities relative to the disolvated magnesium compounds ($\Delta H = -6.0$ and −5.9 kcal/mol, respectively). However, the stabilities of those bromine-containing complexes are somewhat higher than that of $(CH_3)_2Mg$. The complexes of methoxy compounds are much less stable relative the disolvated molecules ($\Delta H = -2.5...-0.7$ kcal/mol). It should be noted that for the disolvated complexes, the values of ΔG considerably differ from the values of ΔE and ΔH, thus indicating a significant contribution of enthropy.

3.4. Disproportionation (Schlenk) Equilibria. The calculated energies for disproportionation equilibria are given in Table 6. The Schlenk equilibrium is shifted toward the formation of CH_3MgX and CH_3OMgX in the gas phase according to our B3LYP/6-31+G* calculations. The relative concentration of magnesium halides should be relatively small, especially in the case of CH_3MgX as the calculated equilibrium constants from eq 5:

$$\Delta G = -RT \ln K \tag{5}$$

are 9.6×10^{-5} (X = Cl) and 2.1×10^{-5} (X = Br). In the case of CH_3OMgX these values are 9.5×10^{-3} (X = Cl) and 1.5×10^{-2} (X = Br), respectively.

The solvation has a strong influence on the Schlenk equilibrium decreasing the endothermicity of disproportionation reactions 2 and 3 but still the predominant species in solution should be CH_3MgX and CH_3OMgX. The effect of solvation is the strongest in the case of CH_3MgCl where the addition of the first solvent molecule diminishes the endothermicity of reaction 2 by 1.06 kcal/mol ($\Delta\Delta H$) and the second solvent molecule has an additional 0.76 kcal/mol effect. For the other studied species the effects are smaller and in case of the alkoxymagnesium halides the second solvent molecule even increases the endothermicity. Nevertheless, the absolute endothermicities are in all cases bigger for the alkylmagnesium halides relative to the alkoxy compounds.

TABLE 5: The NBO Atomic Charges Calculated at the B3LYP/6-31G* Level

	Mg	C	Hal	ΣH	O	N	Phen
$MgCl_2$	+1.587		−0.794				
$MgBr_2$	+1.484		−0.742				
CH_3MgCl	+1.454	−1.369	−0.804	+0.719			
CH_3MgBr	+1.413	−1.371	−0.760	+0.719			
CH_3OMgCl	+1.664	−0.266	−0.815	+0.560	−1.142		
CH_3OMgBr	+1.617	−0.266	−0.770	+0.559	−1.139		
$(CH_3)_2Mg$	+1.370	−1.374		+1.378			
$(CH_3O)_2Mg$	+1.727	−0.263		+1.095	−1.148		
$MgCl_2{\cdot}(CH_3)_2O$	+1.609		−0.818				
$MgBr_2{\cdot}(CH_3)_2O$	+1.527		−0.772				
$CH_3MgCl{\cdot}(CH_3)_2O$	+1.515	−1.394	−0.824	+0.677			
$CH_3MgBr{\cdot}(CH_3)_2O$	+1.482	−1.399	−0.785	+0.680			
$CH_3OMgCl{\cdot}(CH_3)_2O$	+1.660	−0.268	−0.833	+0.532	−1.109		
$CH_3OMgBr{\cdot}(CH_3)_2O$	+1.625	−0.269	−0.794	+0.533	−1.109		
$(CH_3)_2Mg{\cdot}(CH_3)_2O$	+1.454	−1.394		+1.303			
$(CH_3O)_2Mg{\cdot}(CH_3)_2O$	+1.702	−0.268		+1.043	−1.111	-	
$MgCl_2{\cdot}2(CH_3)_2O$	+1.624		−0.831				
$MgBr_2{\cdot}2(CH_3)_2O$	+1.560		−0.795				
$CH_3MgCl{\cdot}2(CH_3)_2O$	+1.561	−1.408	−0.837	+0.640			
$CH_3MgBr{\cdot}2(CH_3)_2O$	+1.533	−1.405	−0.806	+0.639	-	-	
$CH_3OMgCl{\cdot}2(CH_3)_2O$	+1.677	−0.269	−0.845	+0.512	−1.098		
$CH_3OMgBr{\cdot}2(CH_3)_2O$	+1.648	−0.268	−0.810	+0.513	−1.096		
$(CH_3)_2Mg{\cdot}2(CH_3)_2O$	+1.517	−1.401		+1.233	-		
$(CH_3O)_2Mg{\cdot}2(CH_3)_2O$	+1.716	−0.266		+1.001	−1.098		
1,10-phen						−0.415	0.000
$MgCl_2(\text{phen})$	+1.599		−0.836	-		−0.566	+0.073
$MgBr_2(\text{phen})$	+1.578		−0.818	-		−0.562	+0.058
$CH_3MgCl(\text{phen})$	+1.535	−1.389	−0.843	+0.639		−0.542	+0.058
$CH_3MgBr(\text{phen})$	+1.507	−1.394	−0.814	+0.646		−0.550	+0.056
$CH_3OMgCl(\text{phen})$	+1.647	−0.257	−0.849	+0.495	−1.098	−0.554	+0.061
$CH_3OMgBr(\text{phen})$	+1.618	−0.260	−0.818	+0.499	−1.096	−0.556	+0.057
$(CH_3)_2Mg(\text{phen})$	+1.490	−1.364		+1.228		−0.536	+0.010
$(CH_3O)_2Mg(\text{phen})$	+1.684	−0.258		+0.974	−1.095	−0.548	+0.049

TABLE 6: Energies (Δ*E*, contains zero-point vibrational energy (ZPVE) correction), Enthalpies (Δ*H*), and Gibbs Free Energies (Δ*G*) for Disproportionation Equilibria of Methylmagnesium Halides and Methoxymagnesium Halides at B3LYP/6-31+G* Level (All values are given in kcal/mol.)

	Δ*E*	Δ*H*	Δ*G*
$2\mathrm{RMgX} \rightleftharpoons \mathrm{R_2Mg} + \mathrm{MgX_2}$			
CH_3MgCl	5.27	5.08	6.84
CH_3MgBr	5.24	5.15	6.38
CH_3OMgCl	1.95	2.20	2.76
CH_3OMgBr	1.58	1.90	2.47
$2[\mathrm{RMgX{\cdot}(CH_3)_2O}] \rightleftharpoons \mathrm{R_2Mg{\cdot}(CH_3)_2O} + \mathrm{MgX_2{\cdot}(CH_3)_2O}$			
CH_3MgCl	3.89	4.02	3.70
CH_3MgBr	4.52	4.54	4.48
CH_3OMgCl	1.63	1.69	0.88
CH_3OMgBr	2.19	2.24	1.41
$2[\mathrm{RMgX{\cdot}2(CH_3)_2O}] \rightleftharpoons \mathrm{R_2Mg{\cdot}2(CH_3)_2O} + \mathrm{MgX_2{\cdot}2(CH_3)_2O}$			
CH_3MgCl	3.14	3.26	2.70
CH_3MgBr	4.51	4.54	4.40
CH_3OMgCl	1.88	1.88	0.75
CH_3OMgBr	2.40	2.50	2.45
$2\mathrm{RMgX(phen)} \rightleftharpoons \mathrm{R_2Mg(phen)} + \mathrm{MgX_2(phen)}$			
CH_3MgCl	2.76	2.76	3.83
CH_3MgBr	6.05	5.64	7.33
CH_3OMgCl	1.51	1.63	2.89
CH_3OMgBr	1.40	1.55	1.57
$\mathrm{RMgX} + \mathrm{RMgX(phen)} \rightleftharpoons \mathrm{R_2Mg} + \mathrm{MgX_2(phen)}$			
CH_3MgCl	−6.02	−6.53	−4.27
CH_3MgBr	−7.55	−8.17	−5.72
CH_3OMgCl	−3.26	−3.20	−2.20
CH_3OMgBr	−6.65	−6.51	−5.98
$\mathrm{RMgX{\cdot}(CH_3)_2O} + \mathrm{RMgX(phen)} \rightleftharpoons \mathrm{R_2Mg{\cdot}(CH_3)_2O} + \mathrm{MgX_2(phen)}$			
CH_3MgCl	−0.82	−0.82	−0.31
CH_3MgBr	−2.28	−2.48	−1.54
CH_3OMgCl	−1.95	−1.95	−1.51
CH_3OMgBr	−5.14	−5.08	−5.27
$\mathrm{RMgX{\cdot}2(CH_3)_2O} + \mathrm{RMgX(phen)} \rightleftharpoons \mathrm{R_2Mg{\cdot}2(CH_3)_2O} + \mathrm{MgX_2(phen)}$			
CH_3MgCl	3.33	3.33	4.02
CH_3MgBr	4.22	4.01	4.86
CH_3OMgCl	−0.31	−0.31	0.44
CH_3OMgBr	−1.54	−1.44	−1.13

The disproportionation equilibrium should be modified if the solution contains **phen**. In case of excess (or equimolarity) of **phen** over organomagnesium compound the reaction goes as

$$2\mathrm{RMgX(phen)} \rightleftharpoons \mathrm{R_2Mg(phen)} + \mathrm{MgX_2(phen)} \qquad (6)$$

The effect of **phen** on the equilibrium is similar to that of solvation. The reaction is less endothermic except for CH_3MgBr where the influence of **phen** leads to an increase of the endothermicity by 0.49 kcal/mol (ΔΔ*H*). The changes are the greatest for CH_3MgCl where the endothermicity decreases by 2.32 kcal/mol. However, for all the studied species, the equilibrium is still shifted toward the formation of CH_3MgX(phen) or CH_3OMgX(phen).

In the case of titration of a Grignard reagent with an alcohol in the presence of **phen** as an indicator, there is, however, an excess of free RMgX or ROMgX in the solution and the Schlenk equilibria can be written as

$$\mathrm{RMgX{\cdot}}n\mathrm{(CH_3)_2O} + \mathrm{RMgX(phen)} \rightleftharpoons \mathrm{R_2Mg{\cdot}}n\mathrm{(CH_3)_2O} + \mathrm{MgX_2(phen)} \qquad (7)$$

$$\mathrm{ROMgX{\cdot}}n\mathrm{(CH_3)_2O} + \mathrm{ROMgX(phen)} \rightleftharpoons \mathrm{(RO)_2Mg{\cdot}}n\mathrm{(CH_3)_2O} + \mathrm{MgX_2(phen)} \qquad (8)$$

The formation of disproportionation products with reversed complexation, i.e., R_2Mg(phen) and $MgX_2{\cdot}n(CH_3)_2O$, is energetically less favorable. The modified Schlenk equilibria (eqs 7 and 8) are shifted toward the disproportionation products in the gas phase ($n = 0$) and in case of the monosolvated species ($n = 1$) due to the stronger complex between **phen** and magnesium halide. In the case of the disolvated species which are the closest to the situation in real solution, the equilibrium is strongly (even stronger than in the absence of **phen**) shifted toward the nondisproportionated RMgX while for ROMgX the equilibrium is shifted in the opposite direction. As a result, in solution of RMgX in the presence of **phen**, alkylmagnesium halide complexes should prevail. Alkoxymagnesium halides should, in contrast, be strongly disproportionated, especially CH_3OMgBr.

So, according to our calculations, prior to the titration equivalence point, **phen** is complexated with RMgX while after equivalence point the complexes with MgX_2 should prevail. These results indicate that the disappearance of the red color of the complex of **phen** with a Grignard reagent during titration with an alcohol is not due to the complex formation between alkoxymagnesium halide and **phen**. The alkoxy complex disproportionates to a dialkoxymagnesium compound and a magnesium halide, and **phen** gets entirely complexated with the magnesium halide in the equivalence point because the complex between magnesium halide and **phen** is much stronger than that of the other studied complexes. Thus, the complexation of MgX_2 with **phen** in the solution seems to be the reason of the disappearance of the red color of the solution near the titration end point. The absorption spectrum of the complex $MgCl_2$(phen) calculated by the TD/MPW1PW91/6-311+G** method lies in the ultraviolet region (Figure 1f) supporting our hypothesis.

4. Conclusions

Our calculated absorption spectra of the complexes CH_3MgCl(phen) and CH_3OMgCl(phen) by the DFT TD/MPW1PW91/6-311+G** method indicate that the disappearance of the red color of the solution during titration of a Grignard reagent RMgX with an alcohol in the presence of **phen** is not due to the complex formation between alkoxymagnesium halide ROMgX and **phen**. We have investigated disproportionation equilibria, e.g., the Schlenk equilibria, which can be important during titration of the complex RMgX(phen) with an alcohol both in the gas phase and in solution. Solvation was modeled using the supermolecule approach.

The solvation reaction is exothermic for all the studied magnesium compounds—CH_3MgX, CH_3OMgX, MgX_2, $(CH_3)_2Mg$, and $(CH_3O)_2Mg$ (X = Cl, Br). The tricoordinated magnesium is planar in the monosolvated complexes while the tetracoordinated magnesium forms with its ligands a deformed tetrahedron in the disolvated complexes.

The complexes of **phen** with $MgCl_2$ and $MgBr_2$ are the most stable according to our DFT B3LYP/6-31+G* calculations, Δ*H* is −43.9 and −39.8 kcal/mol, respectively. The complexation energy is the lowest in case of the complex of **phen** with $(CH_3)_2Mg$ (Δ*H* = −23.7 kcal/mol). The solvation of studied compounds causes a remarkable decrease in the complexation energies as one of the reagents (magnesium compound) is stabilized by the specific solvation but the product (complex) is not solvated. The solvation has also a strong influence on the disproportionation equilibria.

According to the DFT B3LYP/6-31+G* calculations, prior to the titration equivalence point **phen** is complexated with a Grignard reagent while after the equivalence point the complexation with magnesium halide should be important as the complex between MgX_2 and **phen** is much stronger than the other studied magnesium complexes. Thus, the complexation of MgX_2 with **phen** in the solution seems to be the reason for the disappearance of the red color of the solution. The calculated absorption spectrum of $MgCl_2$(phen) at the DFT TD/MPW1PW91/6-311+G** level of theory confirms the hypothesis.

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