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IR Matrix Isolation and ab Initio Identification of Products of the Reactions of CH_3Cl and CH_3Br with Mg

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IR spectra of products of the reactions of methyl halogen molecules CH_3Cl and CH_3Br with Mg have been studied under matrix isolation conditions. Comparison of the spectra with ab initio frequencies and intensities allows us to identify the primary reaction products as monomagnesium Grignard complexes CH_3MgX (X = Cl, Br) and therefore reject the possibility of creation of energetically more stable bimagnesium species CH_3-MgMgX. Those species according to ab initio calculations should be bound with respect to the decomposition $CH_3MgX + Mg$. Ab initio calculations have been carried out at several levels, including the large basis set MP2 and DFT treatments. The scaling factors, which bring the computed harmonic frequencies into correspondence with the experimental band positions, have been deduced. It is shown that, unlike the majority of organic molecules, organometallic complexes should be considered more carefully, in the sense that the scaling factors of the advanced MP2 and DFT procedures are not as close to unity as is believed.

1. Introduction

Structure and properties of the Grignard reagents have been the subject of much attention and research. The theoretical interest in getting quantitative details on the molecular geometry, energetics, and spectra of methyl−magnesium Grignard reagents CH_3MgX, where X stands for halogen, started with computational work by Baskin et al.[1] and progressed through a series of subsequent calculations and models.[2−7] Experimentally, in 1980 Ault investigated the reactions of CH_3Cl and CH_3Br with Mg under the conditions of low-temperature matrix isolation. Following the IR spectroscopy observations, Ault concluded that metal atoms could react with methylhalogens leading to formation of monometal Grignard reagents CH_3MgX.[8] On the basis of the UV studies of the magnesium atoms and cluster reactions with methylhalogens, Klabunde et al.[9,10] suggested that formation of bimagnesium Grignard reagents CH_3MgMgX, along with CH_3MgX, was expected in these reactions. However, no direct evidence of the creation of such intriguing substances was discovered. Jasien and Dykstra[3,4] have confirmed by ab initio quantum chemistry calculations that bimagnesium reagents are stable species. The same conclusion has been formulated in our more recent ab initio studies of bi- and trimagnesium fluorine Grignard reagents.[6] Predictions of vibrational spectra of mono- and bimagnesium species CH_3-MgMgX along with CH_3MgX (X = F, Cl, Br) at a reasonable accuracy level have been given as well.[6,7]

This paper presents a direct comparison of newly recorded experimental and recomputed theoretical IR spectra of products of the reactions of CH_3Cl and CH_3Br with Mg. One of the goals of the present work is an attempt to answer an intriguing question: whether these reactions may lead to the bimagnesium Grignard compounds $CH_3MgMgCl$ and $CH_3MgMgBr$? The theory predicts that such bimagnesium molecules should be more stable than the corresponding monomagnesium species.[3,4,6,7] Nevertheless, thus far, no direct experimental proof of formation of the bimagnesium reagents has been accomplished. The hopes to approach this goal relied on preliminary calculation results[7] which showed that bi- and monomagnesium Grignard reagents could be distinguished by their IR spectra. However, in order to increase the accuracy of theoretical predictions, we have performed a new high level ab initio quantum chemistry vibrational analysis of reagents and expected products of the reactions studied experimentally. In the course of these calculations, new important lessons have been learned which also warrant discussions.

The next two sections describe the details of the experimental and computational approaches, respectively. Then, we compare our experimental and theoretical data for methylhalogen species. In the following sections 4 and 5 vibrational spectra of the reaction products of CH_3Cl and CH_3Br with Mg are reported. Finally, we discuss the results and conclusions.

2. Experiment

The reactions have been carried out in low-temperature argon matrixes upon cocondensation of Mg with CH_3X and Argon at 12 K. The experiments have been performed with a conventional matrix isolation apparatus (see Figure 1). It includes the cryostat, the closed-cycle refrigerator, the stainless steel metal evaporator with external resistive heating, and the quartz crystal microbalance mounted near the sample window.

The spectra have been recordered in two different modes: (1) UV−vis in the region 240−900 nm and IR in the region 4000−400 cm^{-1} when using the KBr sample and external windows, and (2) only IR in the region 4000−250 cm^{-1} when using the CsI sample and the KRS-5 external windows.

IR spectra were obtained on the Specord-M80 spectrometer with spectral slit 2.5 cm^{-1}, and UV−vis spectra on the Specord-M40 spectrometer with spectral slit 40 cm^{-1}. Magnesium was codeposited with CH_3X/Ar mixtures (CH_3X:Ar = 1:50 or 1:100). The prolongation of deposition was 5−15 min when measuring UV−vis spectra and 180−240 min when measuring IR spectra.

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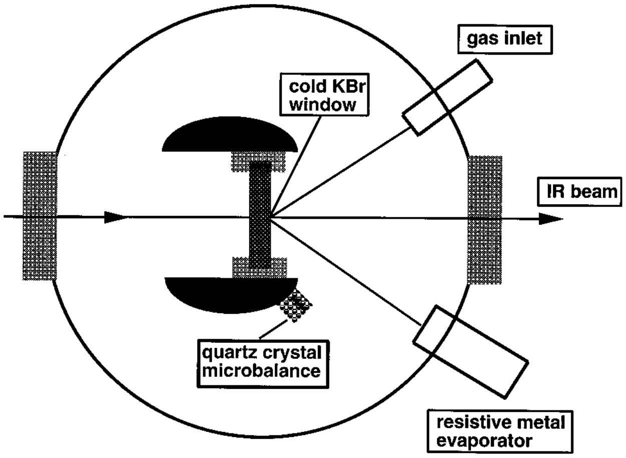

Figure 1. Cross section of the cryostat on the level of sample window.

As was first observed by Ault,[8] the cocondensation led to red-colored matrixes. The UV−vis spectra helped us to recognize that the higher magnesium aggregates formed in the matrixes were responsible for that color. Customary manipulations with the matrixes after the deposition including matrix annealing and UV irradiation by the super-high-pressure Hg lamp have been undertaken. IR spectra of the pure methylhalogen species CH_3Cl and CH_3Br have been recordered and analyzed as well.

3. Calculation Details

As mentioned in the Introduction, the results of ab initio quantum chemistry calculations carried out at the HF/6-31G* and MP2/6-31G* levels for the CH_3MgX and CH_3MgMgX (X = F, Cl, Br) Grignard reagents confirm that the bimagnesium species are more stable than the monomagnesium ones. Additionally, and perhaps more important, bi- and monomagnesium compounds may be distinguished in the mixture by their vibrational spectra.[6,7] It is generally accepted that the harmonic vibrational frequencies computed by ab initio methods can be brought into good agreement with experiment after a proper scaling procedure.[11,12] For the Hartree−Fock level of theory the frequency scaling factors are near 0.89. In the case of Moller−Plessett perturbation theory (MP2) calculation factors closer to unity, about 0.95, are expected.[13]

Although MP2 calculations of harmonic vibrational frequencies and spectral intensities can be routinely carried out, these calculations with fairly large basis sets for molecules containing heavy elements are still computationally demanding. In this work we report the complete geometry optimization and vibrational analysis for the series of species CH_3X, CH_3MgX, and CH_3MgMgX (X = Cl, Br) at the all-electron MP2/6-311++G** level.

An alternative to MP2 or other expensive electron correlation ab initio treatments is density functional theory (DFT). The most popular versions of DFT with respect to modeling vibrational spectra of molecules are the BLYP (based on Becke's exchange functional[14] in combination with the Lee−Yang−Parr correlation functional[15]), B3LYP (with Becke's three-parameter exchange functional[16]), or B3P86 (the three-parameter Becke's exchange functional[16] combined with the Perdew correlation functional[17]). Traditional ab initio basis sets may be used in the DFT calculations. It is believed that convergence with respect to basis set increase is fast in DFT techniques. In this work, in addition to the MP2/6-311++G** results, we show the data obtained with the B3P86/6-311++G** version and, for single species, several DFT results are compared, namely, BLYP/6-311++G**, B3LYP/6-311++G**, and BLYP/TZ94P. The calculations have been done with the Gaussian 94[18] and Dgauss[19] program suites.

Examples of successful applications of DFT procedures for predictions and interpretations of molecular vibrational spectra are numerous. Studies that refer to the published data on combined investigations using theoretical DFT calculations and matrix-isolation experiments are cited in refs 20−24. Careful analyses show that for many organic molecules the vibrational band positions predicted by DFT methods are within 20−50 cm^{-1} of experiment, and the frequency scaling factors for BLYP and B3LYP versions approach unity: 0.995 and 0.963.[13]

4. Results for Methyhalogens. Theory vs Experiment

Figures 22 and 3 show the IR spectra of CH_3Cl and CH_3Br, (i.e., the reaction reagents) isolated in argon matrixes at 12 K. The panels in each of these figures refer to various regions of wavenumbers and demonstrate the most prominent vibrational bands, positions of which are, of course, consistent with the handbook reference data.

Tables 1 and 2 present the detailed comparison of the experimental band positions and theoretical MP2/6-311++G** and B3P86/6-311++G** harmonic frequencies and corresponding IR intensities for the CH_3Cl and CH_3Br molecules.

We see that there is good agreement between the experimental and computed spectra. To be more specific, we notice that an accuracy of about 5−8 cm^{-1} compared to the gas phase, or 20−30 cm^{-1} compared to the condensed phase, is typical for low frequencies. The discrepancies for the C−H stretching frequencies are larger and amount to 100−150 cm^{-1}. As expected, the application of the scaling procedure brings the computed harmonic frequencies into reasonable agreement with the experimental band positions. For the MP2 data the corresponding scaling factors are 0.95−0.96, and for the DFT data the scaling factors approach unity (in both cases). These results are in extremely good agreement with the conclusions of Rauhut and Pulay.[13]

Computed intensities should be helpful in determining positions of the bands: the C−X stretch vibrations are supposed to be the most intense; the symmetrical C−H stretching vibrations are next most intense, and so forth. Although the spectra are calculated for the gas phase, it should be pointed out that the matrix shifts, namely the changes in spectral band positions in the matrix compared to the gas-phase values, are not large in these cases.

5. Structure and Spectra of Reaction Products

Equilibrium structures of the mono- and bimagnesium Grignard complexes have been described in detail in previous publications.[1−7] All of the CH_3MgX or $CH_3MgMg'X$ species possess C_{3v} symmetry with C−Mg distances close to 2.1 Å and Mg−Mg′ distances − 2.9 Å.

Tables 3 and 4 contain the computed vibrational frequencies and IR intensities for the CH_3MgCl, $CH_3MgMgCl$, CH_3MgBr, and $CH_3MgMgBr$ molecules. As referenced previously,[7] these data confirm that the IR spectra of the CH_3MgX and CH_3MgMgX complexes are different, which justifies certain efforts to identify both types (mono and bi) of complexes among the reaction products.

In Figure 4, the spectra of the Mg/CH_3Br/Ar cocondensate in the regions 3200−2700 and 750−400 cm^{-1} are shown. One can see no noticeable changes in the spectra immediately after deposition or after annealing up to 35 K. However, the growth of four bands, indicated by arrows in Figure 4, is obvious in the course of irradiation. The experiments with the Mg/CH_3Cl/Ar cocondensates showed almost the same spectra as was observed for CH_3Br. The bands have different shapes, but they

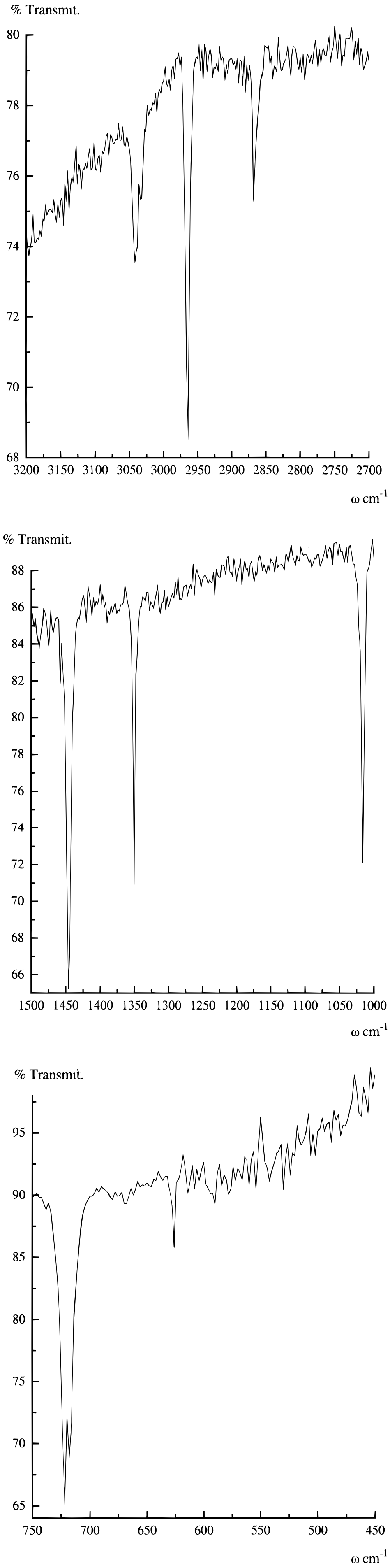

Figure 2. IR spectrum of cocondensate Ar:CH_3Cl (100:1).

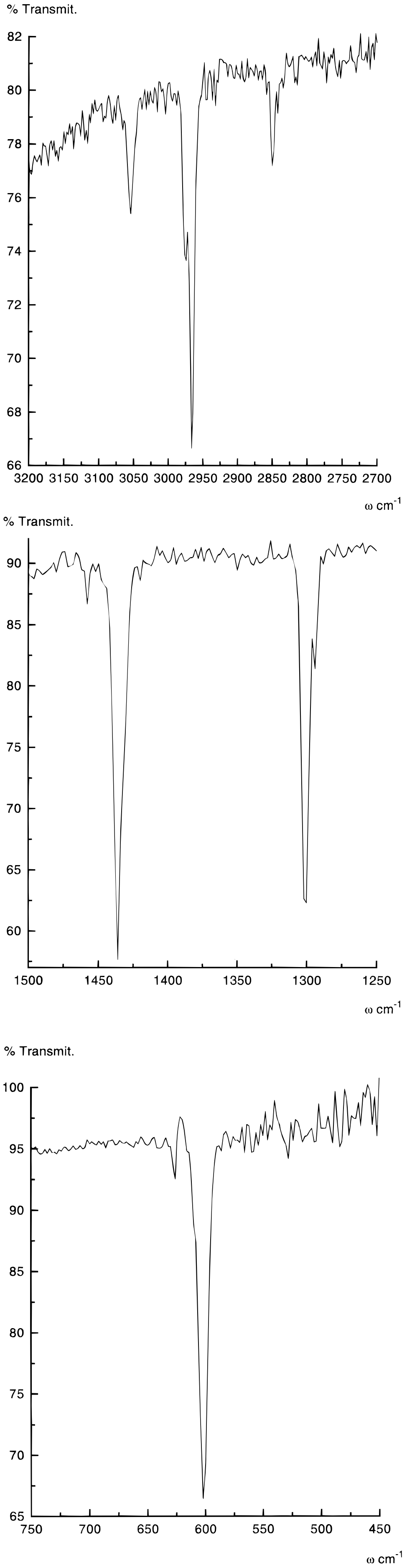

Figure 3. IR spectrum of cocondensate Ar:CH_3Br (100:1).

TABLE 1: Calculated (MP2/6-311++G and B3P86/6-311++G**) and Experimental IR Spectra of CH$_3$Cl[a]**

calculated				experimental (this work)		
MP2		B3P86		gas	matrix CH$_3$Cl:Ar = 1:100	
ω	I	ω	I	ω	ω	assignment
785.8	24	739.7	29	733	722, 718	ν_3(A1)
1065.7	3	1004.1	4	1017	1016	ν_6(E)
1443.1	18	1364.5	12	1354	1350	ν_2(A1)
1491.1	5	1461.6	8	1452	1446	ν_5(E)
3116.2	27	3160.8	24	2968	2964	ν_1(A1)
3223.9	6	3271.7	4	3054	3042, 3033	ν_4(E)

[a] Frequencies (ω) are in cm^{-1}, theoretical intensities (I) in km/mol.

TABLE 2: Calculated (MP2/6-311++G and B3P86/6-311++G**) and Experimental IR Spectra of CH$_3$Br[a]**

calculated				experimental (this work)		
MP2		B3P86		gas	matrix CH$_3$Br:Ar = 1:100	
ω	I	ω	I	ω	ω	assignment
647.1	9	616.7	12	611	602	ν_3(A1)
990.3	5	967.4	6	955	953	ν_6(E)
1382.4	26	1336.2	21	1306	1300	ν_2(A1)
1490.9	5	1468.0	7	1443	1436	ν_5(E)
3119.7	19	3090.4	17	2973	2966	ν_1(A1)
3235.0	3	3202.2	2	3056	3054	ν_4(E)

[a] Frequencies (ω) are in cm^{-1}, theoretical intensities (I) in km/mol.

TABLE 3: Calculated (MP2/6-311++G and B3P86/6-311++G**) Harmonic Frequencies (ω, cm^{-1}) and IR Intensities (I, km/mol) for CH$_3$MgCl and CH$_3$MgMgCl**

CH$_3$MgCl				CH$_3$MgMgCl			
B3P86		MP2		B3P86		MP2	
ω	I	ω	I	ω	I	ω	I
				57.2[a]	17	57.5[a]	19
				120.3[a]	0	118.9[a]	0
117.5[a]	35	112.4[a]	38	186.7	5	190.1	4
371.2	17	383.1	13	474.4	134	492.6	136
598.0[a]	83	588.9[a]	84	546.3[a]	29	537.3[a]	26
632.3	100	645.0	102	559.4	20	564.0	14
1163.6	0	1179.6	0	1151.8	0	1171.5	0
1444.4[a]	0	1455.5[a]	0	1443.5[a]	2	1454.7[a]	2
3027.5	21	3063.9	18	3011.7	52	3042.4	48
3110.1[a]	10	3157.5[a]	12	3092.2[a]	18	3133.9[a]	19

[d] Doubly degenerate frequency.

TABLE 4: Calculated (MP2/6-311++G and B3P86/6-311++G**) Harmonic Frequencies (ω, cm^{-1}) and IR Intensities (I, km/mol) for CH$_3$MgBr and CH$_3$MgMgBr**

CH$_3$MgBr				CH$_3$MgMgBr			
B3P86		MP2		B3P86		MP2	
ω	I	ω	I	ω	I	ω	I
				53.1[a]	13	50.7[a]	14
				119.1[a]	0	108.5[a]	0
108.1[a]	28	101.4[a]	31	160.6	7	163.5	6
300.2	16	305.6	15	409.3	90	419.4	90
595.9[a]	76	589.7[a]	76	546.1[a]	29	537.2[a]	26
609.0	85	612.6	86	556.2	36	559.8	35
1161.0	0	1176.7	0	1151.2	0	1171.1	0
1444.9[a]	0	1456.9[a]	0	1443.2[a]	2	1454.0[a]	2
3027.5	23	3059.3	19	3011.8	54	3042.7	50
3110.8[a]	10	3153.4[a]	12	3092.4[a]	17	3134.3[a]	19

[a] Doubly degenerate frequency.

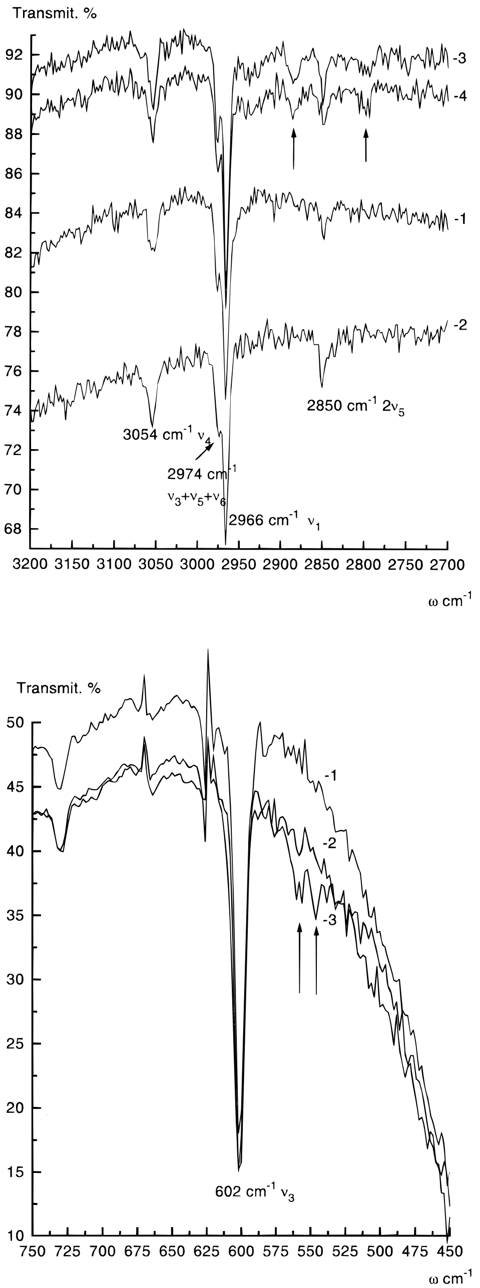

Figure 4. IR spectrum of cocondensate Mg/CH$_3$Br/Ar (1/20/1000). The C−H stretch region (3200−2700 cm^{-1}) and C−Br stretch region (750−450 cm^{-1}) are shown: (1) after deposition; (2) after annealing to 35 K; (3) after 15 min irradiation; (4) after 30 min irradiation.

appear approximately at the same positions and in the similar fashion as in the case of Mg/CH$_3$Br/Ar.

If we compare the experimental spectra with the calculation results (Tables 3 and 4), we notice that, according to these new investigations, the reactions Mg + CH$_3$X (X = Cl, Br) lead to the formation of monomagnesium substances. The most important feature is that we observe a pair of bands of close intensities at 544 and 568 cm^{-1} for Ar/CH$_3$Cl/Mg and at 546 and 558 cm^{-1} for Ar/CH$_3$Br/Mg. This is consistent with the calculation predictions. We believe that these bands belong to bending vibrations of the monomagnesium compounds. We exclude the possibility that the observed bands belong to the bimagnesium compounds. If this were true, we would observe the most intense bands in the region of 400−480 cm^{-1}.

The spectra of other possible secondary reaction products such as CH$_3$Mg, MgX$_2$, and MgX have been computed as well, but none of them have been identified.

6. Discussion and Conclusions

The results described in this work are worth discussion from two viewpoints: the reliability of spectral identification of synthesized Grignard reagents, and the reliability of modern theoretical predictions of vibrational spectra of organometallic compounds of moderate size, such as those considered here.

TABLE 5: Theoretical Vibrational Frequencies (ω, cm^{-1}) and IR Intensities (I, km/mol) for CH_3MgBr Calculated with the MP2 and Different DFT Approaches

MP2/6-311++G**		B3P86/6-311++G**		B3LYP/6311++G**		BLYP/6-311++G**		BLYP/TZ94P	
ω	I	ω	I	ω	I	ω	I	ω	I
101.4[a]	31	108.1[a]	28	108.1[a]	27	104.8[a]	23	87.5[a]	22
305.6	15	300.2	16	296.0	17	287.4	16	282.3	16
589.7[a]	76	595.9[a]	76	600.6	81	580.7	75	585.3	63
612.6	86	609.0	85	601.5[a]	72	594.3[a]	65	607.9[a]	59
1176.7	0	1161.0	0	1168.1	0	1132.7	3	1126.2	2
1457.0[a]	0	1444.9[a]	0	1452.9[a]	0	1419.4[a]	0	1422.1[a]	0
3059.3	9	3027.5	23	3011.7	28	2943.3	30	2958.7	25
3153.4	12	3110.8[a]	10	3085.7[a]	13	3014.2[a]	13	3034.5[a]	12

[a] Doubly degenerate frequency.

With respect to the first issue, we are certain that the species formed under these experimental conditions are the monomagnesium Grignard reagents CH_3MgX, and not the bimetallic complexes CH_3MgMgX (X = Cl, Br). The decisive point is the observation that approximate positions and especially intensities of the IR bands in our spectra, namely pairs of bands at 544 and 568 cm^{-1} for $Ar/CH_3Cl/Mg$, and 546 and 558 cm^{-1} for $Ar/CH_3Br/Mg$, of close IR intensities, are more consistent with the ab initio predictions for CH_3MgX (Tables 3 and 4) than for CH_3MgMgX. If the bimagnesium reagents were formed, for both halogen species the single intense line at lower frequencies that falls in the region carefully studied in this work would dominate in the spectra. According to previous ab initio calculations,[3,4,6,7] formation of the bimagnesium species CH_3MgMgX is an energetically favorable process with respect to the CH_3MgX + Mg channel of reaction, and we could expect creation of these substances in our experiments. However, it is not confirmed by these IR studies. The most reasonable explanation is that the energy barriers for the insertion of the second Mg atom are too high for these reactions.

Another issue is a discrepancy between the results of high-level ab initio calculations and experimental data with respect to vibrational band positions. This conflicting difference is clearly worse than claimed in some recent investigations. If one believes in the scaling procedure, the scaling factors here are not as close to unity for both MP2 and DFT options. Moreover, the different approaches give slightly different qualitative pictures of the spectra taking the CH_3MgBr molecule as an example (see Table 5).

From the data of Table 5 one can see that the ordering of the bands in the 600 cm^{-1} region, referring to the CH_3 rocking (doubly degenerate within the C_{3v} symmetry) and C−Mg stretch vibrations, depends on the calculation method used. The MP2 and B3P86 (the Perdew correlation functional) as well as the Hartree−Fock[2,6,7] approximations place the rocking frequency lower than that of C−Mg stretch, but the DFT methods with another correlation functional (e.g., Lee−Yang−Parr type) predict the opposite trend. For the main goal of this work, namely the spectroscopic identification of the Grignard reagents, this difference is not critical. The most important conclusion here is that all the versions predict for CH_3MgX two bands near 600 cm^{-1} of very close IR intensities. In addition, the spectral patterns of CH_3MgX and CH_3MgMgX are sharply different. This example illustrates the qualitative dependence of DFT results on the choice of the correlation functional.

Analysis of the data collected in Table 5 also shows that the discrepancies in predictions of band positions between these MP2 and DFT approaches (treated on equal grounds) lie within 5.7% for the lowest frequency, 1.4% for the highest frequency, 0.8% for the CH_3 rocking, and 1.9% for the C−Mg stretch frequencies. Therefore, the expected error bars for the bands predicted by these ab initio methods are estimated as 5(10) cm^{-1} in the 600 cm^{-1} region and 45 cm^{-1} in the 3000 cm^{-1} region.

TABLE 6: Scaling Factors Which Bring into Correspondence the Computed with the MP2/6-311++G and B3P86/6-311++G** Approaches Harmonic Frequencies and the Observed Spectral Bands (ν, cm^{-1}) of the CH_3MgCl and CH_3MgBr Species**

CH_3MgCl			CH_3Br + Mg		
ν	MP2	B3P86	ν	MP2	B3P86
544	0.92	0.91	546	0.92	0.92
568	0.88	0.90	558	0.91	0.92
2794	0.91	0.92	2798	0.91	0.92
2884	0.91	0.92	2886	0.92	0.93

Making a direct comparison of computed theoretical and experimental vibrational frequencies of the CH_3MgCl and CH_3MgBr species, we can deduce the scaling factors (Table 6) which bring the ab initio harmonic predictions to correspondence with the experimental fundamentals. One should notice almost uniform values 0.91−0.93 for these compounds.

The conclusion of such an analysis is that for these organometallic compounds even modern correlation treatments should be corrected with the help of scaling factors to a larger extent than in the case of simple organic molecules. We should recall that for CH_3Cl and CH_3Br our calculations allow us to deduce scaling factors of 0.95 for MP2/6-311++G** and about 1.0 for B3P86/6-311++G**, in accordance with literature data.[13]

One should take into consideration the influence of the matrix on the spectra, namely the matrix shifts, as a possible contribution to the experimental versus theoretical discrepancies. For the reaction reagents CH_3Cl and CH_3Br, the matrix shifts are within 2 cm^{-1} for the CH_3-rocking bands and within 20 cm^{-1} for the high-frequency region of the stretch C−H vibrations (see Tables 1 and 2). These corrections, when applied for the Grignard complexes, will not change the deduced scaling factors. The only chance is that for the molecules CH_3MgCl and CH_3MgBr, the matrix shifts are considerably larger. since the insertion of metal atoms changes the character of bonding properties considerably.[6,7] This is reflected by shifts of the frequency values themselves from the parent methylhalogen molecules (for example, for the CH_3-rocking: 1017 cm^{-1} in CH_3Cl (536 cm^{-1} in CH_3MgCl, 955 cm^{-1} in CH_3Br (546 cm^{-1} in CH_3MgBr). Noticeable vibrational matrix shifts may be expected for the C−Mg stretch frequencies. This analysis requires further studies.

The final results of this work may be formulated in short as follows: First, a new attempt to synthesize bimagnesium Grignard reagents by reactions Mg + CH_3X (X = Cl, Br) under the matrix isolation conditions did not lead to their direct observation. According to the IR spectra of the reaction products, only monomethylmagnesium Grignard complexes CH_3MgX are formed. Second, we have deduced scaling factors which bring into agreement the harmonic frequencies computed by ab initio techniques (MP2 and DFT with large basis sets) with the experimental fundamental frequencies. These factors

(0.91−0.93) are smaller for the studied organometallic compounds than those (0.95−0.99) generally accepted for organic molecules.

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References and Notes

(1) Baskin, C. P.; Bender, C. E.; Lucchese, R. R.; Bauschlicher, C. W.; Schaefer, H. F. *J. Mol. Struct.* **1976**, *32*, 125.

(2) Sakai, S.; Jordan, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 4019.

(3) Jasien, P. J.; Dykstra, C. E. *J. Am. Chem. Soc*. **1983**, *105*, 2089.

(4) Jasien, P. J.; Dykstra, C. E. *J. Am. Chem. Soc*. **1985**, *107*, 1891.

(5) Davis, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 4145.

(6) Nemukhin, A. V.; Topol, I. A.; Weinhold, F. *Inorg. Chem*. **1995**, *34*, 2980.

(7) Nemukhin, A. V.; Solov'ev, V. N.; Sergeev, G. B.; Topol, I. A. *Mendeleev Commun.* **1996**, No. 1, 5.

(8) Ault, B. S. *J. Am. Chem. Soc.* **1980**, *102*, 3480.

(9) Imuzu, Y.; Klabunde, K. J. *Inorg. Chem.* **1984**, *23*, 3602.

(10) Klabunde, K. J.; Whetten, A. *J. Am. Chem. Soc.* **1986**, *408*, 6529.

(11) Fogarasi, G.; Pulay, P. *Annu. Rev. Phys. Chem.* **1984**, *35*, 191.

(12) Fogarasi, G.; Pulay, P. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: Amsterdam, 1985; Vol. 14.

(13) Rauhut, G.; Pulay, P. *J. Phys. Chem.* **1995**, *99*, 3093.

(14) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098.

(15) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B41*, 785.

(16) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648.

(17) Perdew, J. P. *Phys. Rev.* **1986**, *33*, 8822.

(18) *Gaussian 94*, Revision D.4; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P.M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(19) Andzelm, J.; Wimmer, E. *J. Chem. Phys.* **1992**, *96*, 508.

(20) Martin, J. M. L.; Van Alsenoy, C. *J. Phys. Chem.* **1996**, *100*, 6973.

(21) Tremblay, B.; Roy, P.; Manceron, L.; Alikhani, M. E.; Roy, D. *J. Chem. Phys.* **1996**, *104*, 2773.

(22) Andrews, L.; Chertikhin, G. V.; Ricca, A.; Bauschlicher, C. W. *J. Am. Chem. Soc.* **1996**, *118*, 467.

(23) Andrews, L.; Chertikhin, G. V.; Thompson, A.; Dillon, J.; Byrne, S.; Bauschlicher, C. W. *J. Phys. Chem*. **1996**, *100*, 10088.

(24) Galan, F.; Fouassier, M; Tranquille, M.; Mascetti, J.; Papai, I. *J. Phys. Chem. A* **1997**, *101*, 2626.