

FULL PAPER

Density-Functional Study of (Solvated) Grignard Complexes

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Received: 19 November 1999/ Accepted: 24 January 2000/ Published: 28 February 2000

Abstract Density Functional calculations have been used to study the solvent effect of diethyl ether on the Schlenk equilibrium and the aggregation of Grignard reagents RMgX with $\text{R} = \text{Me, Et, Ph}$. Solvent stabilization of the Mg complexes of the first solvent is larger than that of the second one. The solvation energy decreases on going from the dihalides MgX_2 to the monohalides RMgX to the diorganyl compounds MgR_2 . The calculations indicate that the energetic preference of the unsymmetrical species reduces upon solvation. The strong tendency to dimerization of the un- and partly solvated compound vanishes for the higher solvated cases.

Keywords Grignard compounds, Diethylether, Schlenk equilibrium, DFT calculation, Solvent effects

Introduction

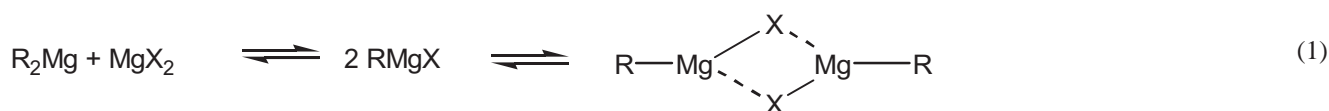
Since its discovery nearly a century ago, the Grignard reagent has been a workhorse in synthetic organic chemistry for the formation of carbon-carbon bonds. In spite of its popular use, mechanistic insight into the formation and reactions of Grignard reagents is trailing.[1] Theoretical calculations can provide such insight. This approach was stimulated by the work of Skell and Girard[2] who reported the reaction of ground-state magnesium with alkyl halides by means of matrix deposition in 1972. In 1980 Ault[3] provided the first spectroscopic characterization of the unsolvated Grignard species CH_3MgX ($\text{X} = \text{Cl, Br, I}$), formed by codeposition of Mg and CH_3X at 15 K. The low tem-

perature matrix reactions are not restricted to magnesium atoms only. Matrix isolation studies performed by Klabunde *et al.* [4] are indicative of a higher reactivity for magnesium clusters. Smirnov and Tyurina [5] have reviewed the role of magnesium clusters in the formation and reactions of Grignard reagents. In a recent matrix infrared study, Bare and Andrews used isotopic substitution and density functional theoretical (DFT) calculations to assign the reaction products formed from methyl halides and laser-ablated magnesium atoms.[6] Many of the theoretical studies on Grignard reagents concern the methyl halides,[7] while some address the ethylene derivatives.[8] They typically do not incorporate the effects of solvents,[9] even though the influence of the solvent on the Schlenk equilibrium and the formation of oligomers (Eq. 1) can be pronounced.

In a recent study Tuulmets and Panov showed that Grignard reagents form partly solvated species $\text{RMgCl}\cdot n(\text{solvent})$ ($n \leq 1$) in hydrocarbon solutions with diethyl ether being the most effective Lewis base. The structures of these complexes remain to be determined. The au-

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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday



thors also reported that strong solvation favors disproportionation and that steric hindrance by bulky organyl groups favors formation of unsymmetrical species.[10]

In the present study we investigate the influence of the degree of solvation on the structures, the Mg-C bond strength, and the energetics of the equilibria that the Grignard reagent RMgX ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$; $\text{X} = \text{Cl}, \text{Br}$) is involved in. We use diethyl ether as solvent as most Grignard reactions are performed in either diethyl ether or THF.

Methods and computational details

The calculations were carried out with the Amsterdam-Density-Functional (ADF) program package.[11] The molecular orbitals were expanded in an uncontracted set of Slater-type orbitals (STOs) containing diffuse functions. The basis set is of triple- ζ quality, augmented with one polarization function, i.e., 2p on H, 3s on C and O, 3p on Mg, 4s on Cl, and 5s on Br. The basis set superposition error (BSSE) is expected to be negligible for this large basis set.[12] The frozen-core approximation (C, O, Mg, 1s; Cl, 1s-2p; Br, 1s-3p) was used throughout.[13]. All geometry optimizations were carried out without imposing symmetry constraints. While various conformations exist for the solvated species, we believe to have obtained to most stable ones - an exhaustive conformational search for each system is beyond the scope of this study. The numerical integrations were performed with the procedure developed by Baerends *et al.*[14] Energies were evaluated using the local spin density approximations including Becke's nonlocal corrections to the exchange energy, together with the Vosko-Wilk-Nusair (VWN) parameterization with

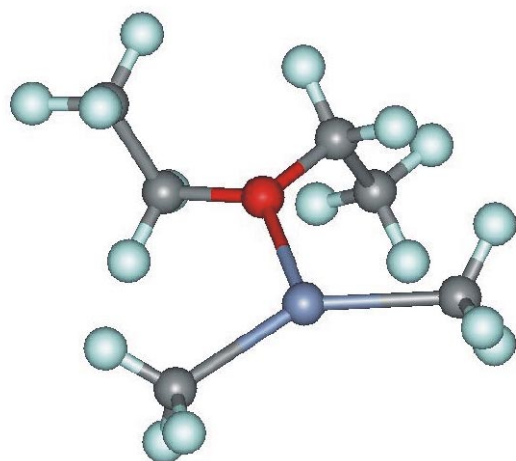


Figure 1 Molecular Structure of $\text{Me}_2\text{Mg}\cdot\text{Et}_2\text{O}$

Perdew's nonlocal corrections to the correlation energy self-consistently.[15]

Results and discussion

We discuss first molecular structures of the Grignard reagents, then the Mg-insertion reaction, followed by an evaluation of the energetics of the (un)solvated systems. Next, the Schlenk equilibrium, dimerization of the Grignard reagent, vibrational analysis, and the Mg-C bond strength are addressed.

Molecular geometries of Grignard reagents

All unsolvated compounds have, as expected, linear structures with sp -hybridized magnesiums. Selected bond lengths of the optimized geometries are given in Appendix 1. Those of MeMgCl agree well with earlier theoretical data.[7,16b] Comparison of the structural parameters shows that the Mg-C bond lengthens successively on replacing Ph for Me for Et, while their Mg-X ($\text{X} = \text{Cl}, \text{Br}$) bonds are longer than those of the corresponding magnesium halides MgX_2 .

None of the structures of the Et_2O solvated organomagnesium compounds possess any symmetry (C_1). Coordination to the solvent molecule lengthens both the Mg-C and Mg-X bonds (Appendix 1). All monosolvated structures contain an essentially planar tricoordinated magnesium (Figure 1). This trigonal planar geometry is also found in the crystal structure of bis(trimethylsilyl)methylmagnesium chloride (diethyl etherate).[17] The steric bulk of the SiMe_3 group prevents coordination of a second solvent molecule.

The structures of the compounds disolvated by Et_2O have a distorted tetrahedral arrangement around magnesium (Figure 2). Coordination by a second solvent molecule lengthens the Mg-C and Mg-X bonds by nearly twice the amount of that due to the first one. Similar structures were reported for Me_2O disolvated structures with a 2.283 Å long Mg-Cl bond for $\text{MgCl}_2\cdot 2\text{Me}_2\text{O}$ and Mg-C and Mg-Cl bond lengths of 2.135 Å and 2.315, respectively, for $\text{MeMgCl}\cdot 2\text{Me}_2\text{O}$. [16] The theoretically predicted bond lengths compare well with reported [18] experimental bond lengths (shown in parenthesis in Appendix 1).

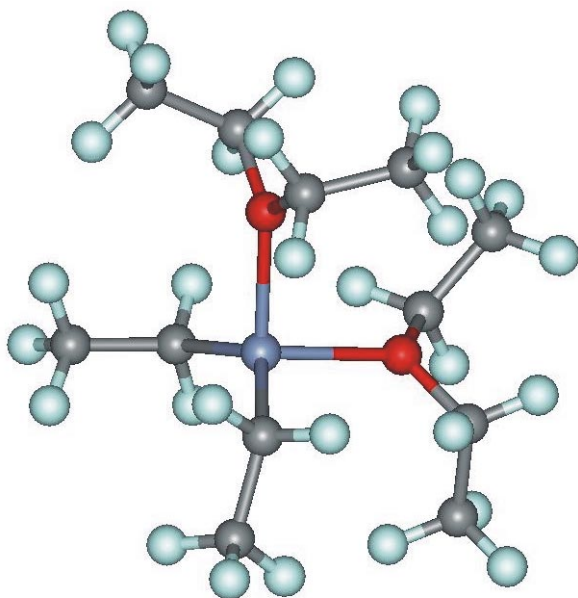
Energetics for magnesium insertion

Reaction energies for the insertion of Mg into the C-X bond are obtained from the energies of the starting halides, magnesium, and the Grignard reagents, and are listed in Table 1.

Table 1 Calculated reaction energies for the reaction of magnesium with organyl halides

Reaction	ΔH (kJ·mol ⁻¹)
MeCl + Mg \longrightarrow CH ₃ MgCl	-218.37
MeBr + Mg \longrightarrow CH ₃ MgBr	-216.94
EtCl + Mg \longrightarrow EtMgCl	-187.89
EtBr + Mg \longrightarrow EtMgBr	-187.96
PhCl + Mg \longrightarrow PhMgCl	-202.58
PhBr + Mg \longrightarrow PhMgBr	-206.24

Insertion of Mg into MeCl is calculated to be exothermic by 218.4 kJ mol⁻¹, which compares well with earlier values ranging from -219 to -227 kJ mol⁻¹. [7, 8] The sensitivity of the reaction energy to the nature of the organic group rather than that of the halide (Cl vs Br), is evident from the 30.5 kJ mol⁻¹ less exothermic Mg-insertion into EtCl, which illustrates that the Mg-C bond is more stabilized by the more electron donating group. Davis *et al.* reported a reaction energy of -227 kJ mol⁻¹ (MP2/6-31G*) for the insertion of Mg into chloroethylene, [8] which is only slightly higher than that for the insertion into MeCl, despite the shorter and hence stronger Mg-C bond of vinylmagnesium chloride. [13] Using ADF we calculate a reaction energy of -204 kJ mol⁻¹ for the Mg-insertion into chloroethylene. [8] The Mg-insertion reactions into PhX (X = Cl, Br) are 14.7 and 18.3 kJ mol⁻¹, respectively, more exothermic than those for the corresponding EtX.

**Figure 2** Molecular Structure of Et₂Mg·2Et₂O**Table 2** Calculated solvation ΔE (kJ·mol⁻¹) energies by diethylether for magnesium compounds

RMgX + Et ₂ O \longrightarrow RMgX·Et ₂ O			
MgCl ₂	-99.6	MeMgCl	-71.4
MgBr ₂	-96.0	MeMgBr	-73.0
Me ₂ Mg	-49.3	EtMgCl	-70.0
Et ₂ Mg	-44.3	EtMgBr	-68.5
Ph ₂ Mg•	-51.6	PhMgCl	-74.1
		PhMgBr	-73.9
RMgX·Et ₂ O + Et ₂ O \longrightarrow RMgX·2Et ₂ O			
MgCl ₂	-68.5	MeMgCl	-48.4
MgBr ₂	-67.5	MeMgBr	-45.5
Me ₂ Mg	-32.0	EtMgCl	-46.3
Et ₂ Mg	-32.9	EtMgBr	-49.4
Ph ₂ Mg•	-48.8	PhMgCl	-55.6
		PhMgBr	-56.2
RMgX + 2Et ₂ O \longrightarrow RMgX·2Et ₂ O			
MgCl ₂	-168.1	MeMgCl	-119.8
MgBr ₂	-163.5	MeMgBr	-118.5
Me ₂ Mg	-81.3	EtMgCl	-116.3
Et ₂ Mg	-77.2	EtMgBr	-117.9
Ph ₂ Mg•	-100.4	PhMgCl	-129.7
		PhMgBr	-130.1

Solvation energies for magnesium compounds

All MgX₂, R₂Mg, and RMgX (X = Cl, Br; R = Me, Et, Ph) species have significant solvation energies, as is evident from the DFT calculated Et₂O mono- and disolvation energies listed in Table 2. The average monosolvation energies range from 98, 72 to 46 kJ mol⁻¹ for MgX₂, RMgX, and R₂Mg, respectively, with corresponding values of 68, 50, and 40 kJ mol⁻¹ for solvation by an additional Et₂O molecule. As expected, the effect of the first Et₂O solvent molecule is larger than that of the second one. The overall Et₂O solvation energies are substantial and amount to about 166 for MgX₂, 118 for RMgX (R = Me, Et), 128 for PhMgX, 79 for R₂Mg (R = Me, Et), and 100 kJ mol⁻¹ for Ph₂Mg. The solvent stabilization is largest for the magnesium halides and least for the diorganyl magnesium compounds with intermediate values for the Grignard reagents. Solvent stabilization of phenyl derivatives is evidently about 10 kJ mol⁻¹ per phenyl group larger than for the magnesium compounds containing alkyl groups. There is hardly any difference in solvation energies between compounds carrying Me or Et groups as well as those having Cl or Br substituents.

Bock and coworkers reported HF/6-31G* solvation energies of 248, 193 and 153 kJ mol⁻¹ for reactions (1), (2), and (3), respectively, using the simpler Me₂O molecule instead of diethylether. [16b] Our solvation energies, using Et₂O as solvent molecule, are considerably smaller with corresponding values of 168, 120, and 81 kJ mol⁻¹. We presume these differences of ca. 75 kJ mol⁻¹ to originate mainly from the

Table 3 Calculated energies ($\text{kJ}\cdot\text{mol}^{-1}$) for the Schlenk equilibrium for the unsolvated and solvated Grignards reagents CH_3MgX , EtMgX and PhMgX ($X = \text{Cl}, \text{Br}$)

$2 \text{RMgX} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2$			
MeMgCl	22.3	MeMgBr	21.7
EtMgCl	24.9	EtMgBr	24.3
PhMgCl	16.6	PhMgBr	14.5
$2 \text{RMgX}\cdot\text{Et}_2\text{O} \rightleftharpoons \text{R}_2\text{Mg}\cdot\text{Et}_2\text{O} + \text{MgX}_2\cdot\text{Et}_2\text{O}$			
MeMgCl	16.1	MeMgBr	21.0
EtMgCl	21.0	EtMgBr	21.1
PhMgCl	18.6	PhMgBr	17.9
$2 \text{RMgX}\cdot 2\text{Et}_2\text{O} \rightleftharpoons \text{R}_2\text{Mg}\cdot 2\text{Et}_2\text{O} + \text{MgX}_2\cdot 2\text{Et}_2\text{O}$			
MeMgCl	12.5	MeMgBr	13.9
EtMgCl	12.2	EtMgBr	14.4
PhMgCl	3.5	PhMgBr	5.4

effects of electron correlation. Differences in the BSSE, which is known to be very small for the method used in this study,[12] is another possible contribution but also steric effects of the differently sized solvent molecules (Et vs Me) may have a profound impact.

- (1) $\text{ClMgCl} + 2\text{Me}_2\text{O} \rightarrow \text{ClMgCl}\cdot 2\text{Me}_2\text{O}$
- (2) $\text{MeMgCl} + 2\text{Me}_2\text{O} \rightarrow \text{MeMgCl}\cdot 2\text{Me}_2\text{O}$
- (3) $\text{MeMgMe} + 2\text{Me}_2\text{O} \rightarrow \text{MeMgMe}\cdot 2\text{Me}_2\text{O}$

The Schlenk equilibrium

Grignard reagents, diorganylmagnesium, and dihalomagnesium compounds are related to each other by the Schlenk equilibrium. The energies for the equilibria of the various un-, mono- and disolvated systems are given in Table 3. All disproportionations are slightly endothermic (3.5 to 24.9 $\text{kJ}\cdot\text{mol}^{-1}$), favoring the Grignard reagent, but this energetic preference reduces on solvent complexation, particularly for PhMgX . The endothermicity of the Schlenk equilibrium for the unsolvated alkyl Grignard reagents is ca. 23 $\text{kJ}\cdot\text{mol}^{-1}$ and ca. 8 $\text{kJ}\cdot\text{mol}^{-1}$ for the phenyl derivatives. The DFT calculated value of 22.3 $\text{kJ}\cdot\text{mol}^{-1}$ for unsolvated MeMgCl is in agreement with that of 23.8 $\text{kJ}\cdot\text{mol}^{-1}$ reported at MP4SDTQ/6-31G**//RHF/6-31G*.[16b] Interestingly, complexation with only one diethyl ether shifts the equilibrium of the phenyl Grignard reagents toward the unsymmetrical species, while the opposite is the case for the aliphatic derivatives, giving a combined average endothermicity of 19 $\text{kJ}\cdot\text{mol}^{-1}$. With an additional solvent molecule all disproportionations become clearly less endothermic, with values of 14 and 4 $\text{kJ}\cdot\text{mol}^{-1}$ for the alkyl and phenyl Grignard reagents, respectively.

The reported reaction enthalpies ΔH for the Schlenk equilibrium in diethyl ether, determined by calorimetry, of 15.6

Table 4 Calculated dimerization energies ($\text{kJ}\cdot\text{mol}^{-1}$) for selected Grignard reagents by halide bridging

$2 \text{RMgX} \longrightarrow [\text{RMgX}]_2$			
MgCl_2	-152.8	MgBr_2	-138.6
Me_2Mg	-79.8	Et_2Mg	-69.3
Ph_2Mg	-110.0		
MeMgCl	-139.5	MeMgBr	-126.2
EtMgCl	-138.1	EtMgBr	-125.2
PhMgCl	-147.5	PhMgBr	-134.6
$2 \text{RMgX}\cdot\text{Et}_2\text{O} \longrightarrow [\text{RMgX}\cdot\text{Et}_2\text{O}]_2$			
$\text{MgCl}_2\cdot\text{Et}_2\text{O}$	-139.8	$\text{MgBr}_2\cdot\text{Et}_2\text{O}$	-134.5
$\text{Me}_2\text{Mg}\cdot\text{Et}_2\text{O}$	-73.9	$\text{Et}_2\text{Mg}\cdot\text{Et}_2\text{O}$	-70.8
$\text{Ph}_2\text{Mg}\cdot\text{Et}_2\text{O}$	-99.6		
MeMgCl $\cdot\text{Et}_2\text{O}$	-111.0	MeMgBr $\cdot\text{Et}_2\text{O}$	-93.9
EtMgCl $\cdot\text{Et}_2\text{O}$	-113.7	EtMgBr $\cdot\text{Et}_2\text{O}$	-101.5
PhMgCl $\cdot\text{Et}_2\text{O}$	-126.0	PhMgBr $\cdot\text{Et}_2\text{O}$	-119.9
$2 \text{RMgX}\cdot 2\text{Et}_2\text{O} \longrightarrow [\text{RMgX}\cdot\text{Et}_2\text{O}]_2 + 2 \text{Et}_2\text{O}$			
$\text{MgCl}_2\cdot 2\text{Et}_2\text{O}$	-2.8	$\text{MgBr}_2\cdot 2\text{Et}_2\text{O}$	11.9
MeMgCl $\cdot 2\text{Et}_2\text{O}$	-14.2	MeMgBr $\cdot 2\text{Et}_2\text{O}$	-2.9
EtMgCl $\cdot 2\text{Et}_2\text{O}$	-21.1	EtMgBr $\cdot 2\text{Et}_2\text{O}$	-4.2
PhMgCl $\cdot 2\text{Et}_2\text{O}$	-14.8	PhMgBr $\cdot 2\text{Et}_2\text{O}$	0.5

$\text{kJ}\cdot\text{mol}^{-1}$ for EtMgBr and 8.5 $\text{kJ}\cdot\text{mol}^{-1}$ for PhMgBr,[19] are in excellent agreement with our theoretically determined values of 18.4 and 5.4 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. Earlier estimates, using THF as solvent, gave reaction enthalpies of -25.5 and -11.8 $\text{kJ}\cdot\text{mol}^{-1}$, respectively.[20] It has been suggested that the difference in the Schlenk equilibrium between diethyl ether and THF results from the increased coordination number of magnesium bromide in THF.[21] From NMR spectroscopic analysis values of -13.3 $\text{kJ}\cdot\text{mol}^{-1}$ [22] and -18.7 $\text{kJ}\cdot\text{mol}^{-1}$ [23] have been reported for PhMgBr. Bock *et al.* estimated an endothermicity of 15.1 $\text{kJ}\cdot\text{mol}^{-1}$ for the Schlenk equilib-

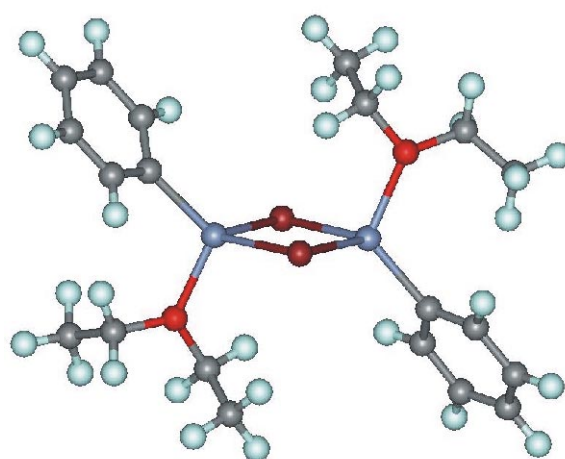
**Figure 3** Molecular Structure of $[\text{PhMgBr}\cdot\text{Et}_2\text{O}]_2$

Table 5 Calculated normal mode vibrational frequencies (in cm^{-1}) of selected magnesium species

	MgCl₂	MgBr₂	EtMgCl	EtMgBr	PhMgCl	PhMgBr
C–Mg [a]	–	–	533.5	521.2	550.0	533.4
Mg–X [a]	306.8/439.1	224.2/367.9	335.1	265.8	350.0	276.7
C(X)–Mg–X [b]	94.8	66.2	108.16	100.2	110.7	103.8
	MgCl₂·Et₂O	MgBr₂·Et₂O	EtMgCl·Et₂O	EtMgBr·Et₂O	PhMgCl·Et₂O	PhMgBr·Et₂O
C–Mg [a]	–	–	554.6	543.8	575.8	558.2
Mg–X [a]	340.7/449.5	260.0/380.7	352.0	284.5	368.3	298.7
C(X)–Mg–X [b]	159.7	98.1	175.5	157.1	205.4	168.4

[a] Stretch. [b] Bending

rium of $\text{MeMgCl}\cdot 2\text{Me}_2\text{O}$, [16b] which agrees well with our value of 12.5 kJ mol^{-1} for the Et_2O disolvated complex.

Association of Grignard reagents

An ebulliscope investigation of a variety of Grignard reagents showed that the degree of association is affected by several factors. [24] They are mostly monomeric in THF, but dimers are observed in diethyl ether at higher concentrations. While the degree of aggregation can be determined in solution, this is not the case for the molecular geometry, which is therefore usually assumed to resemble that in the solid state. As expected, the electron deficient Grignard reagent forms a dihalide-bridged dimer not only in the absence of solvent but also in the presence of an equivalent of Et_2O (Figure 3). Selected structural parameters are given in Appendix 2. The unsolvated dimers have Mg–Cl bonds of 2.42 \AA and Mg–Br bonds of about 2.58 \AA , which, however, expand on complexation with Et_2O slightly. These solvated dimers contain tetrahedral magnesiums with relatively short Mg–O bonds of ca. 2.09 to 2.14 \AA . The dimers have Mg–Mg separations of about 3.4 \AA ($X = \text{Cl}$) and 3.6 \AA ($X = \text{Br}$).

The dihalide-bridged isomers are considered to be the most stable dimers. [16b] Our DFT calculations, summarized in Table 4, confirm the substantial exothermicity for dimerization of MgX_2 , RMgX , and R_2Mg . The dimerization energy for all chlorides is ca. 13 kJ mol^{-1} larger than that of the bromides. For the non-bridging substituents the exothermicity decreases in the order $\text{Cl} > \text{Br} > \text{Ph} > \text{Et}, \text{Me}$, with values ranging from $152.8 \text{ kJ mol}^{-1}$ for MgCl_2 to $125.2 \text{ kJ mol}^{-1}$ for EtMgBr . The same trend is found for the Et_2O monosolvated species but with slightly smaller dimerization energies, ranging from $139.8 \text{ kJ mol}^{-1}$ for $\text{MgCl}_2\cdot\text{Et}_2\text{O}$ to 93.9 kJ mol^{-1} for $\text{EtMgBr}\cdot\text{Et}_2\text{O}$. The MP4SDTQ/6-31G* value of $155.1 \text{ kJ mol}^{-1}$ for MeMgCl , reported by Bock and coworkers, [16b] is in reasonable agreement with our DFT value of $138.6 \text{ kJ mol}^{-1}$. These energy data strongly support the claim by Panov *et al.* [10] that partly solvated Grignard reagents $\text{RMgCl}\cdot n\text{Et}_2\text{O}$

($n \leq 1$) tend to form aggregates. The dimerization energy by far exceeds that for the Schlenk equilibrium.

Sharply different results are obtained for the disolvated species $\text{MgX}_2\cdot 2\text{Et}_2\text{O}$ and $\text{RMgX}\cdot 2\text{Et}_2\text{O}$. Due to the elimination of two molecules of Et_2O their dimerizations are nearly thermoneutral, especially for the Br-containing Grignard reagents, which range from -4.2 kJ mol^{-1} for $\text{EtMgBr}\cdot 2\text{Et}_2\text{O}$ to $+0.5 \text{ kJ mol}^{-1}$ for $\text{PhMgBr}\cdot 2\text{Et}_2\text{O}$. Apparently, the energy demanding cleavage of two dative Mg–O bonds, to eliminate the extra solvent molecules, balances the stabilization resulting from dimerization. Bock and coworkers [16] showed the dimerization of $\text{MeMgCl}\cdot 2\text{Me}_2\text{O}$ to be endothermic by 23.4 kJ mol^{-1} at MP2/6-31G*, which compares reasonably well with our DFT value of 14.2 kJ mol^{-1} for the Et_2O disolvated system. They also showed the dimerization of the simpler $\text{HMgCl}\cdot 2\text{Me}_2\text{O}$ to be exothermic by 31.4 kJ mol^{-1} , which, however, on inclusion of entropic effects and thermal corrections becomes exothermic by a modest ΔG° of -21 kJ mol^{-1} . Slightly negative Gibbs energies are also expected for the dimerization of the disolvated Grignard reagents of the present study, although such calculations were beyond our means.

Finally, the question arises how the Schlenk equilibrium is influenced by the association of the Grignard reagents. As mentioned earlier, bridging through the halogen is favored above bridging through the carbon atoms, i.e. the dimerization energy for the pure organyl magnesium dimers is lower than for the mixed ones. Thus, energy is lost upon forming $[\text{R}_2\text{Mg}]_2$ in the Schlenk equilibrium. On the other hand, the dimerization energy is the highest for the binary magnesium halides and energy is gained upon forming $[\text{MgX}_2]_2$. However, the net effect is more or less balanced and the Schlenk equilibrium is only slightly influenced by the association. Taking the calculated dimerization energies of the monosolvated compounds of type $\text{RMgX}\cdot\text{Et}_2\text{O}$ into account and renormalizing for the stoichiometry of the equations used in Table 3 gives values of 19.9 and $15.3 \text{ kJ}\cdot\text{mol}^{-1}$ for the Schlenk equilibrium of $\text{PhMgCl}\cdot\text{Et}_2\text{O}$ and $\text{PhMgBr}\cdot\text{Et}_2\text{O}$, respectively. Since the dimerization energies for the binary alkyl derivatives are even lower than those of the phenyl complexes, comproportionation is slightly more favored due to aggrega-

Table 6 Calculated bond dissociation energies of the Mg–C bond (in kJ·mol⁻¹) of some selected Grignards reagents

D_0	MeMgCl 257.6	MeMgBr 256.0	EtMgCl 221.7	EtMgBr 220.0	PhMgCl 278.2	PhMgBr 275.8
D_0	MeMgCl·2Et₂O 290.2	MeMgBr·2Et₂O 289.7	EtMgCl·2Et₂O 250.8	EtMgBr·2Et₂O 252.3	PhMgCl·2Et₂O 320.7	PhMgBr·2Et₂O 321.1

tion for R = Me, Et. Considering the dimerization energies gives values of 20.4 and 17.9 kJ·mol⁻¹ for the Schlenk equilibrium of MeMgCl·Et₂O and MeMgBr·Et₂O, respectively. The corresponding values for ethyl complexes are 29.4 and 24.7 kJ·mol⁻¹.

Vibrational analysis

The DFT method is being used increasingly for determining accurate harmonic frequencies of (transition) metal complexes. Because only few vibrational studies on Grignard reagents have been reported,[3,25] we report the most characteristic frequencies for un- and monosolvated magnesium compounds (Table 5).

The calculated Mg–C stretching mode of 522–575 cm⁻¹ for the Grignard reagents RMgX (R = Et, Ph; X = Cl, Br) varies with the R- and X-substituents and with the presence of a solvent molecule. The Mg–Br frequencies are at 266–299 cm⁻¹ and those for Mg–Cl at 335–368 cm⁻¹. The bromides have lower Mg–C stretch frequencies than the chlorides and the phenyl derivatives have higher ones than the ethyl magnesium halides, both of which are in line with the calculated bond lengths. Solvation increases the Mg–C and the Mg–X stretching frequencies both by ca. 24 and 19 cm⁻¹, respectively.

Limited data are available to validate the accuracy of these DFT frequencies. In 1980, Ault studied unsolvated MeMgX (X = Cl, Br, I), generated from the reaction of Mg with MeX and trapped in an argon matrix, and reported three to four vibrational frequencies.[3] The 530 cm⁻¹ band was assigned to a symmetric MeMgCl umbrella mode deformation. Jordan *et al.* [7] questioned this assignment and suggested it to be the C–Mg–Cl bending mode or alternatively the Mg–C stretch for which they calculated an SCF frequency of 647 cm⁻¹. However, our DFT calculated Mg–C stretch of 533 cm⁻¹ for EtMgCl is in perfect agreement with the frequency at 530 cm⁻¹. The DFT calculated Mg–C and Mg–Br stretches of 544 and 285 cm⁻¹, respectively, for EtMgBr·2Et₂O are also in reasonable agreement with the 485–506 and 248 cm⁻¹ observed by Kress and Novak [25] for EtMgBr solvated in diethyl ether and THF. Our data differ from those of Pratt and Khan, who recently calculated the Mg–Cl stretching frequency of MeMgCl to increase from 366 to 372 cm⁻¹ on Et₂O monosolvation with a concurrent decrease of the Mg–C frequency from 642.8 to 605.8 cm⁻¹. [16]

The magnesium-carbon bond strength

The Mg–C bond dissociation energies, $D_0(\text{Mg–C})$, were calculated for the Grignard reagents RMgX (R = Et, Ph; X = Cl, Br) and their Et₂O disolvated forms (Table 6). The sizeable Mg–C bond strength is insensitive to the nature of the halide but varies instead with the organic group and strengthens on solvation. The Ph–Mg bond is ca. 70 kJ mol⁻¹ stronger than the Et–Mg bond and is enhanced by ca. 40 kJ mol⁻¹ on solvation, giving a C–Mg bond strength for PhMgBr·2Et₂O of 322 kJ mol⁻¹.

Only limited experimental information is available for comparison, because thermochemical studies of Grignard compounds are hampered by the Schlenk equilibrium. Thus, THF solutions of phenylmagnesium bromide also contain diphenylmagnesium, but the Schlenk equilibrium could be determined from variable temperature ¹H or ¹³C NMR spectroscopy from which subsequently an estimated Mg–C bond strength of 200.0 kJ mol⁻¹ could be determined.[26] We note that the stabilization of Grignard reagents is larger in THF than in diethyl ether. This notion is supported by the experimentally determined value of 226 kJ mol⁻¹ for the Mg–C bond in neopentylmagnesium bromide,[27] which compares well with our DFT calculated bond strengths. The much smaller $D_0(\text{Mg–C})$ value of 134 ± 5 kJ mol⁻¹ for monomeric diorganylmagnesium indicates that the Mg–C bond of diorganylmagnesium compounds is much weaker than that of the Grignard reagents.[28]

Conclusions

Density functional theoretical calculation of molecular geometries, vibrational frequencies, and C–Mg bond energies of the Grignard reagents RMgX (R = Me, Et, Ph; X = Cl, Br) and their diethyl ether mono- and di-solvent complexes show reasonable to good agreement with available experimental and *ab initio* data.

The calculated parameters show that the Mg–C bond lengthens successively on replacing Ph for Me for Et, while their Mg–X (X = Cl, Br) bonds are longer than those of the corresponding magnesium halides MgX₂. Coordination to a Et₂O solvent molecule lengthens both the Mg–C and Mg–X bonds. This effect is reinforced by a second solvent molecule.

The average solvation energies decrease from MgX₂ via RMgX to R₂Mg, with effect of the first Et₂O solvent mol-

ecule being larger than that of the second one. Solvent stabilization of phenyl derivatives is evidently larger than that for the magnesium compounds containing alkyl groups.

All disproportionations are predicted to be slightly endothermic, favoring the Grignard reagent, but this energetic preference reduces on solvent complexation, particularly for PhMgX. The Schlenk equilibrium is only slightly influenced by the strong tendency for aggregation of the Grignard reagents, since the dimerization energies decrease in the order $[R_2Mg]_2 < [RMgX]_2 < [MgX_2]_2$ with a higher tendency for aggregation of the chlorides over those of the bromides.

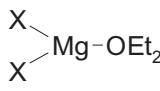
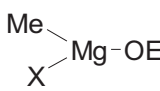
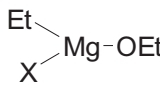
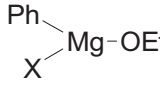
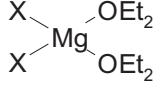
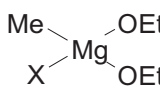
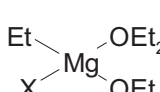
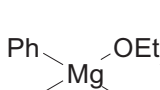
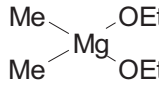
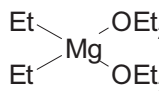
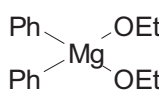
Acknowledgement This investigation was supported in part by the Council of Chemical Sciences (CW) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supplementary material available. The 3D coordinates of $Me_2Mg \cdot Et_2O$, $Et_2Mg \cdot 2Et_2O$ and $[PhMgEt_2O]_2$ are available in PDB format.

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Appendix 1 Selected bond length (Å) of mono- and disolvated magnesium compounds

	C-Mg	X = Cl Mg-X	Mg-O	C-Mg	X = Br Mg-X	Mg-O
X—Mg—X	-	2.191	-	-	2.344	-
Me—Mg—X	2.089	2.219	-	2.087	2.366	-
Et—Mg—X	2.100	2.222	-	2.105	2.371	-
Ph—Mg—X	2.076	2.212	-	2.093	2.371	-
	-	2.227/ 2.238	2.072	-	2.394/ 2.401	2.069
	2.110	2.269	2.089	2.118	2.246	2.098
	2.126	2.268	2.098	2.123	2.421	2.096
	2.103	2.260	2.072	2.105	2.421	2.075
	-	2.289/ 2.310	2.172/ 2.181	-	2.468/ 2.450	2.191 (2.13[a]) 2.200 (2.16)
	2.124	2.305	2.135/ 2.145	2.134	2.473	2.144 2.157
	2.142	2.319	2.145/ 2.131	2.145 (2.15)	2.487 (2.48)	2.132 (2.03) 2.146 (2.05)
	2.127	2.305	2.119/2.133	2.123 (2.20)	2.468 (2.44)	2.123 (2.01) 2.126 (2.06)
Me—Mg—Me	2.112			2.155 / 2.156		2.173 / 2.181
Et—Mg—Et	2.129 / 2.131			2.173 / 2.179		2.173 / 2.184
Ph—Mg—Ph	2.097 / 2.106			2.142 / 2.153		2.141 / 2.167

[a] Dimer. For References see [30,31,32,33]

Appendix 2 Calculated molecular geometry, bond lengths of the halogen-bridged dimeric Grignard reagents

Bond length	C–Mg	Mg–X	Mg–O	Mg–Mg
[MeMgCl] ₂	2.094	2.418	–	3.355
[MeMgBr] ₂	2.093	2.578	–	3.486
[EtMgCl] ₂	2.104	2.421	–	3.361
[EtMgBr] ₂	2.121	2.584	–	3.513
[PhMgCl] ₂	2.081	2.409	–	3.315
[PhMgBr] ₂	2.089	2.573	–	3.471
[MeMgCl·Et ₂ O] ₂	2.118	2.436	2.129	3.363
[MeMgBr·Et ₂ O] ₂	2.122	2.621	2.136	3.568
[EtMgCl·Et ₂ O] ₂	2.130	2.442	2.129	3.425
[EtMgBr·Et ₂ O] ₂	2.131	2.625	2.137	3.610
[PhMgCl·Et ₂ O] ₂	2.114	2.432	2.093	3.437
[PhMgBr·Et ₂ O] ₂	2.120	2.597	2.091	3.641