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Theoretical Study of Magnesium Compounds: The Schlenk Equilibrium in the Gas Phase and in the Presence of Et_2O and THF Molecules

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The Schlenk equilibrium involving RMgX, R_2Mg, and MgX_2 (R = Me, Et, Ph and X = Cl, Br) has been studied both in the gas phase and in diethyl ether (Et_2O) and tetrahydrofuran (THF) solutions by means of the density functional theory (DFT) B3LYP/6-31+G* method. Solvation was modeled using the supermolecule approach. The stabilization due to interaction with solvent molecules decreases in the order $MgX_2 > RMgX > R_2Mg$ and among the groups (R and X) Ph > Me > Et and Cl > Br. Studied magnesium compounds are more strongly solvated by THF compared to Et_2O. The magnesium halide is solvated with up to four solvent molecules in THF solution, assuming that *trans*-dihalotetrakis(tetrahydrofurano)magnesium(II) complex forms. The formation of *cis*-dihalotetrakis(tetrahydrofurano)magnesium(II) is energetically less favorable than the formation of corresponding disolvated complexes. The predominant species in the Schlenk equilibrium are RMgX in Et_2O and $R_2Mg + MgX_2$ in THF, which is consistent with experimental data.

1. Introduction

Although the stoichiometry of a Grignard reagent[1] can be expressed as RMgX (R = organic group, X = halogen), the real composition of the reagent is far more complex, both in solution and in the solid state. It should be expressed by equilibrium of the type

$$(RMgX)_2 \rightleftharpoons 2RMgX \rightleftharpoons R_2Mg + MgX_2 \rightleftharpoons R_2Mg{\cdot}MgX_2 \qquad (1)$$

where the middle part is known as the Schlenk equilibrium[2] and the associated species can exist as dimers, as well as trimers and higher aggregates. The Schlenk equilibrium is dynamic and can be shifted very fast.

The position of the Schlenk equilibrium depends on the solvent, the concentration of the solution, the nature of the organic group, and the halide as well as the temperature. The most important factors are solvent and concentration. All alkyl- and arylmagnesium chlorides, bromides, and iodides are monomeric in tetrahydrofuran (THF) over a wide concentration range (0.1−3.5 M).[3−5] Alkyl- and arylmagnesium bromides and iodides contain essentially monomeric species at low concentrations (less than 0.1 M) and dimeric species at higher concentrations (0.5−1.0 M) in diethyl ether (Et_2O). The alkylmagnesium chlorides are essentially dimeric even at the low concentrations.[3−6a] The difference in Grignard reagent association behavior in THF and Et_2O is attributed to the relative Lewis basicities of the two solvents. Solvent−metal bonding competes with the bridging characteristics of the halide, and THF competes more favorably than Et_2O. The associated complexes are believed to bridge predominantly through halide substituents.[3,5] Variable temperature NMR studies indicate that the rate of alkyl exchange is a function of the structure of the alkyl group, e.g., methyl group exchange is much faster than *t*-butyl group exchange. Temperature effects on the composition of Grignard reagents in solution can be either kinetic or thermodynamic. Increasing temperature usually results in a faster exchange of ligands among magnesium complexes, which translates to faster equilibration rates.[3,4,7a,b] Thus, all factors which affect the position of equilibrium are in close connection with one another.

The Schlenk equilibrium constant is usually expressed as

$$K_S = \frac{[RMgX]^2}{[R_2Mg]{\cdot}[MgX_2]} \qquad (2)$$

If $[R_2Mg] \approx [MgX_2]$, which is frequently the case, a determination of the ratio $[RMgX]/[R_2Mg]$ can be used. The equilibrium constants are also calculated from the equation

$$\Delta G = -RT \ln K \qquad (3)$$

where R is the universal gas constant (8.314 J/mol·K) and T is temperature.

The Schlenk equilibrium has been the subject of various experimental investigations. Calorimetric studies of the heats of reaction between MgX_2 and R_2Mg in dilute solutions of Et_2O[8a−c] and THF[9] (thermochemical titration) have provided thermodynamic parameters and equilibrium constants for several systems. A number of constants, thermodynamic parameters, and qualitative kinetic data for the exchange process have been obtained by variable temperature NMR spectroscopy.[7a−d] Also IR-spectroscopy,[10] polarography,[11] analysis of kinetic investigations of Grignard reactions,[12a,b] and molecular weight measurements[6a,b] have been used.

Several theoretical studies about the Schlenk equilibrium, solvent effects, association processes in Grignard reagents, etc. have been carried out by semiempirical calculations, using the extended Hückel MO[13] (solvents are Me_2O and Me_3N) and CNDO/2[14] (only gas-phase calculations) methods. Calculations have also been carried out by high-level ab initio calculations, using both Hartree−Fock (HF) and Møller−Plesset (MP)

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perturbation calculations[15] (solvent is Me_2O) and density functional theory (DFT), where solvent is Me_2O[16] or Et_2O.[17]

Many crystallographic data are available for the structures of solvated monomeric magnesium compounds.[18−22] The structure in solution, however, can be different from the solid-state structure because of various intermolecular and intramolecular forces in these phases. In the current work we report the results of the density functional theory (DFT) calculations about the Schlenk equilibrium of RMgX, R_2Mg, and MgX_2 ($R = Me$, Et, Ph and $X = Cl$, Br) in the gas phase and in solution. We have used the most common reaction media for Grignard reagents, diethyl ether (Et_2O) and tetrahydrofuran (THF), as solvents.

2. Computational Methods

The calculations were carried out using the GAUSSIAN 98[23] program package. All geometry optimizations and vibrational analyses were done using the density functional theory (DFT) with hybrid B3LYP functional and the 6-31+G* basis set (B3LYP/6-31+G*). 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 energies.

Solvation was modeled using the supermolecule approach, which is the best method to describe the specific solvent effects. Up to two molecules of diethyl ether and up to four molecules of tetrahydrofuran were added to the studied species.

The stability of the solvated species was calculated considering the basis set superposition error (BSSE) estimated according to the counterpoise (CP) correction.[24] The BSSE arises from the mathematical fact that the basis sets are not complete and it should be considered in the case of complexation energies. The dimer (complex) energy minus the monomer energies is the directly calculated complexation energy, $\Delta E_{\mathrm{complexation}}$.

$$\Delta E_{\mathrm{complexation}} = E(\mathrm{AB})^*_{ab} - E(\mathrm{A})_a - E(\mathrm{B})_b \qquad (4)$$

To estimate how much of this complexation energy is due to BSSE, four additional energy calculations were needed. The CP correction is defined as

$$\Delta E_{\mathrm{CP}} = E(\mathrm{A})^*_{ab} + E(B)^*_{ab} - E(\mathrm{A})^*_a - E(\mathrm{B})^*_b \qquad (5)$$

where $E(\mathrm{A})^*_{ab}$ and $E(\mathrm{B})^*_{ab}$ are the monomer energies with the basis set of complex, $E(\mathrm{A})^*_a$ and $E(\mathrm{B})^*_b$ are the monomer energies with their normal basis sets. In all cases the monomers were calculated with the geometry they have in complex. The counterpoise corrected complexation energy, ΔE_{BSSE}, is given as

$$\Delta E_{\mathrm{BSSE}} = \Delta E_{\mathrm{complexation}} - \Delta E_{\mathrm{CP}} \qquad (6)$$

The BSSE was also taken into account in the case of the reactions of the Schlenk equilibrium. The BSSE had a particularly strong influence on both the solvation energies and the Schlenk equilibrium of the bromine-containing compounds compared to the corresponding chlorine compounds, indicating somewhat less satisfactory description of bromine basis set.

3. Results and Discussion

3.1. Structures of Solvated Magnesium Compounds. The optimized structures of some mono- and disolvated species are shown in Figure 1. The monosolvated structures contain an essentially planar tricoordinated magnesium (Figure 1a,b). The tetracoordinated magnesium forms with its ligands a deformed tetrahedron in the disolvated species (Figure 1c,d), in accordance with X-ray diffraction studies of the crystal structures of monomeric $EtMgBr\cdot 2Et_2O$,[18a,b] $PhMgBr\cdot 2Et_2O$ and $Ph_2Mg\cdot 2Et_2O$,[19] $MgBr_2\cdot 2Et_2O$,[20] and $PhMgBr\cdot 2THF$.[21] The geometry of diethyl ether both in the monosolvated and disolvated species is like a "propeller", similar to that obtained by Lammertsma's group.[17] For the solid state, and possibly for the solution state as well, the structure of solvated magnesium compounds depends primarily on the steric requirements of the R group and solvent molecules attached to the magnesium atom. As tetrahydrofuran is sterically less demanding than diethyl ether, magnesium halide can probably coordinate at least four tetrahydrofurans, e.g., $MgBr_2\cdot 4THF$, based on crystallographic data[22a,b] and conclusions by Smith and Becker about their

TABLE 1: Selected Bond Lengths of Solvated Magnesium Compounds at the B3LYP/6-31+G* Level[a]

$Z\cdot nEt_2O$

	r(Mg−O)		r(Mg−X)		r(Mg−C)	
	$n = 1$	$n = 2$	$n = 1$	$n = 2$	$n = 1$	$n = 2$
$MgCl_2$	2.038	2.091	2.238	2.286		
$MgBr_2$	2.046	2.091	2.380	2.427		
MeMgCl	2.085	2.137; 2.140	2.269	2.319	2.104	2.129
MeMgBr	2.089	2.131; 2.140	2.411	2.469	2.102	2.123
EtMgCl	2.088	2.138; 2.141	2.270	2.319	2.119	2.142
EtMgBr	2.087	2.129; 2.140	2.411	2.467	2.117	2.139
PhMgCl	2.075	2.122; 2.126	2.259	2.309	2.108	2.139
PhMgBr	2.082	2.116; 2.120	2.395	2.452	2.102	2.128
Me_2Mg	2.137	2.190			2.127	2.154
Et_2Mg	2.138	2.201			2.144	2.168
Ph_2Mg	2.104	2.157; 2.161			2.125	2.156

$Z\cdot n$THF

	r(Mg−O)		r(Mg−X)		r(Mg−C)	
	$n = 1$	$n = 2$	$n = 1$	$n = 2$	$n = 1$	$n = 2$
$MgCl_2$	2.033	2.075	2.237	2.286		
$MgBr_2$	2.038	2.068	2.379	2.426		
MeMgCl	2.078	2.118; 2.123	2.268	2.321	2.103	2.129
MeMgBr	2.078	2.114; 2.115	2.410	2.467	2.102	2.121
EtMgCl	2.078	2.122; 2.123	2.269	2.322	2.118	2.142
EtMgBr	2.078	2.111; 2.119	2.410	2.469	2.116	2.135
PhMgCl	2.063	2.107; 2.110	2.259	2.313	2.106	2.136
PhMgBr	2.067	2.100; 2.101	2.395	2.460	2.103	2.131
Me_2Mg	2.128	2.170			2.127	2.154
Et_2Mg	2.129	2.172			2.143	2.169
Ph_2Mg	2.099	2.130; 2.145			2.124	2.153; 2.157

$Z\cdot n$THF

	r(Mg−O)	r(Mg−X)	r(Mg−C)
	$n = 3$	$n = 3$	$n = 3$
$MgCl_2$	2.205 (a) 2.097 (e)	2.340 (e)	
$MgBr_2$	2.198 (a) 2.203 (a) 2.073 (e)	2.471 (e) 2.475 (e)	

$Z\cdot n$THF

	r(Mg−O)		r(Mg−X)		r(Mg−C)	
	cis, $n = 4$	*trans*, $n = 4$	*cis*, $n = 4$	*trans*, $n = 4$	*cis*, $n = 4$	*trans*, $n = 4$
$MgCl_2$	2.235 (a) 2.240 (a) 2.322 (e) 2.323 (e)	2.199	2.409 (e)	2.429 2.432		
$MgBr_2$	2.222 (a) 2.298 (e)	2.191	2.551 (e)	2.577 2.579		

[a] All distances are in angstroms, Å.

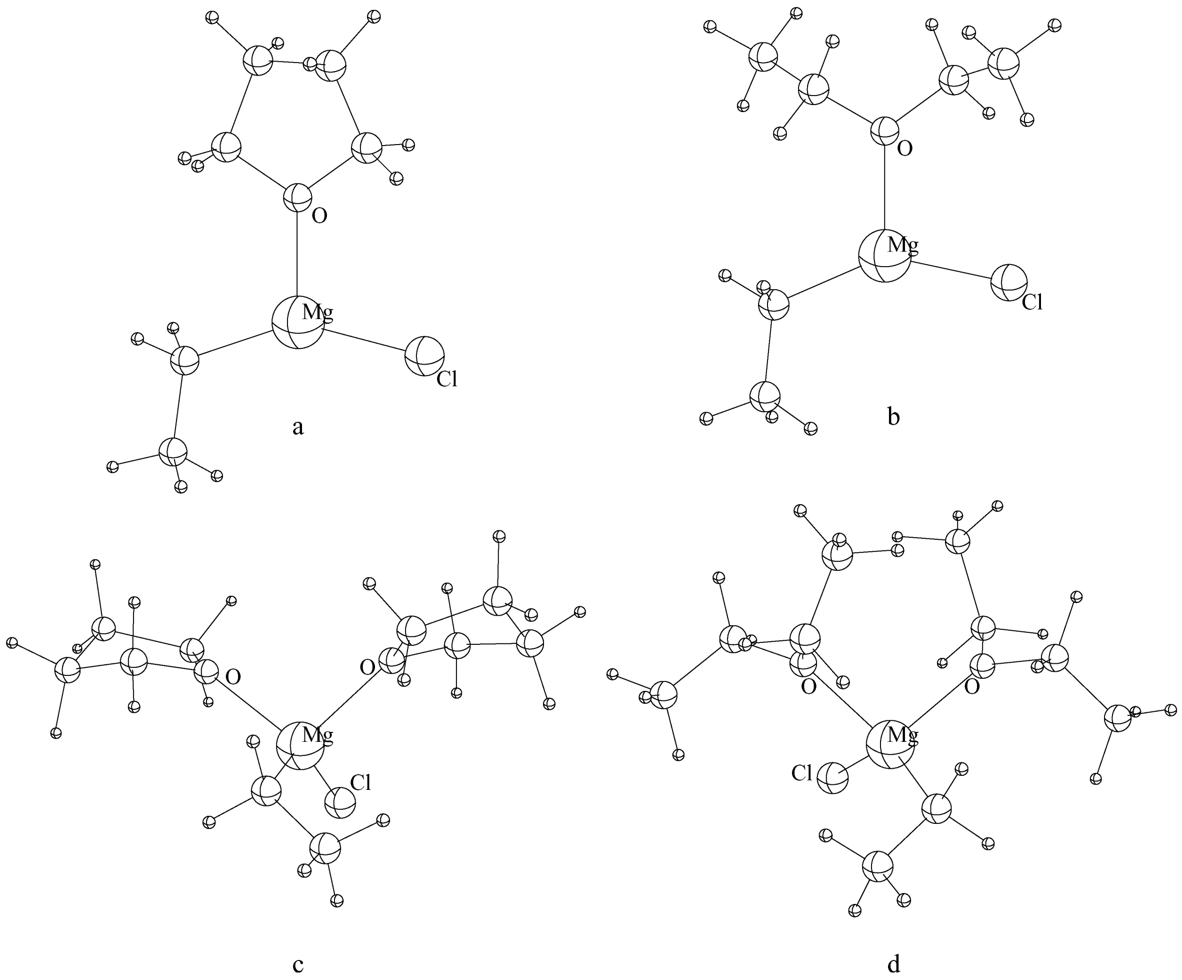

Figure 1. Optimized (at B3LYP/6-31+G* level of theory) structures of monosolvated and disolvated species: (a) EtMgCl·THF, (b) EtMgCl·Et$_2$O, (c) EtMgCl·2THF, and (d) EtMgCl·2Et$_2$O.

TABLE 2: Solvation Energies (Δ*E*, contains zero-point vibrational energy (ZPVE) correction), Enthalpies (Δ*H*), and Gibbs Energies (Δ*G*) of Magnesium Compounds with One or Two Diethyl Ether Molecules at the B3LYP/6-31+G* Level[a]

$Z + nEt_2O \rightarrow Z \cdot nEt_2O$

	Δ*E*		Δ*H*		Δ*G*	
Z	$n = 1$	$n = 2$	$n = 1$	$n = 2$	$n = 1$	$n = 2$
MgCl$_2$	−21.6	−35.3	−21.6	−34.9	−11.7	−14.3
MgBr$_2$	−18.0	−30.1	−17.9	−29.8	−8.2	−8.1
MeMgCl	−14.9	−23.8	−14.6	−23.2	−5.4	−3.7
MeMgBr	−13.0	−21.1	−12.7	−20.6	−3.2	0.7
EtMgCl	−14.8	−23.5	−14.4	−22.9	−4.2	−1.5
EtMgBr	−13.0	−21.1	−12.6	−20.4	−2.2	1.7
PhMgCl	−16.3	−26.7	−15.9	−26.1	−6.3	−4.3
PhMgBr	−13.9	−22.8	−13.6	−22.2	−3.2	0.3
Me$_2$Mg	−9.6	−14.3	−9.4	−13.8	0.4	7.3
Et$_2$Mg	−9.5	−13.5	−9.2	−13.0	1.9	10.0
Ph$_2$Mg	−12.9	−19.4	−12.5	−18.6	−2.3	3.2

[a] All values are in kcal/mol and include BSSE corrections.

calorimetric studies.[9] The optimized structures of tri- and tetrasolvated tetrahydrofuranate complexes of MgCl$_2$ are shown in Figure 2. The tris-tetrahydrofuranate complex of magnesium halide forms a deformed trigonal bipyramid, wherein the chlorine atoms and one THF molecule are equatorial (e) and two THF molecules are axial (a). The tetrakis-tetrahydrofuranate complex of magnesium halide can exist in two forms, as *cis*-dihalotetrakis(tetrahydrofurano)magnesium(II) and *trans*-dihalotetrakis(tetrahydrofurano)magnesium(II). The cis form is a deformed octahedron and as the chlorine atoms are located alongside, we label them as equatorial (e). Thus, two THF ligands are equatorial (e) and the other two THF ligands are axial (a). The trans form is also an octahedron, where equatorial and axial positions are indistinguishable.

The obtained bond lengths of mono- and disolvated magnesium compounds (Table 1) can evidently be related to a lesser steric hindrance to the interaction between the magnesium atom and the oxygen atom(s) of the solvent. The distances between the magnesium atom and the oxygen atom(s) of the solvent increase in the order MgX$_2$ < RMgX < R$_2$Mg and among the groups Ph < Me ≈ Et. The bond lengths r(Mg−O) are somewhat unsymmetrical in the case of disolvated RMgX compounds, $\Delta r = 0.003-0.011$ Å in the Et$_2$O complexes, and $\Delta r = 0.001...0.008$ Å in the THF complexes. The bond lengths r(Mg-X) increase in the direction MgX$_2$ < RMgX (Ph < Me ≈ Et) and r(Mg−C) in the direction RMgX < R$_2$Mg (Ph ≈ Me < Et). The r(Mg−O) is shorter in the case of THF complexes, e.g., $\Delta r = 0.005-0.015$ Å in the monosolvated, and $\Delta r = 0.016-0.029$ Å in the disolvated THF complexes compared to the corresponding Et$_2$O complexes, while r(Mg-X) and r(Mg−C) are more or less constant. All bond lengths are longer in the case of disolvated Et$_2$O and THF complexes compared to the monosolvated complexes. The Mg-X bond lengthens in MgX$_2$·nTHF complexes with the addition of the next THF molecule. The asymmetry of the Mg−O bonds also appears in *tris*- and *cis*-tetrakis-tetrahydrofuranate complexes. The axial Mg−O bonds are somewhat longer than the

TABLE 3: Solvation Energies (Δ*E*, contains zero-point vibrational energy (ZPVE) correction), Enthalpies (Δ*H*), and Gibbs Energies (Δ*G*) of Magnesium Compounds with One to Four Tetrahydrofuran Molecules at the B3LYP/6-31+G* Level[a]

$Z + nTHF \rightarrow Z\cdot nTHF$

Z	Δ*E*		Δ*H*		Δ*G*	
	n = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2
$MgCl_2$	−25.5	−44.0	−25.5	−43.7	−15.9	−22.7
$MgBr_2$	−22.1	−39.3	−21.9	−39.0	−13.0	−17.8
MeMgCl	−18.7	−32.2	−18.4	−31.6	−9.1	−11.5
MeMgBr	−17.0	−29.8	−16.5	−29.2	−7.7	−7.9
EtMgCl	−18.6	−31.9	−18.3	−31.2	−8.1	−9.9
EtMgBr	−17.0	−29.7	−16.6	−29.0	−7.2	−7.2
PhMgCl	−20.3	−35.7	−20.0	−35.1	−9.8	−13.3
PhMgBr	−18.1	−33.0	−17.8	−32.2	−6.8	−10.3
Me_2Mg	−13.3	−22.5	−13.1	−22.0	−3.2	−0.5
Et_2Mg	−13.4	−22.2	−13.1	−21.7	−1.8	1.8
Ph_2Mg	−16.7	−28.6	−16.3	−27.8	−5.6	−5.9
	n = 3		*n* = 3		*n* = 3	
$MgCl_2$	−49.2		−48.6		−15.7	
$MgBr_2$	−43.4		−42.8		−8.9	
	cis, *n* = 4	*trans*, *n* = 4	*cis*, *n* = 4	*trans*, *n* = 4	*cis*, *n* = 4	*trans*, *n* = 4
$MgCl_2$	−43.6	−52.9	−42.8	−51.6	3.9	−7.0
$MgBr_2$	−37.7	−46.2	−37.0	−45.5	11.0	3.1

[a] All values are in kcal/mol and include BSSE corrections.

TABLE 4: Energies (Δ*E*, contains zero-point vibrational energy (ZPVE) correction), Enthalpies (Δ*H*), and Gibbs Energies (Δ*G*) of Displacement of Diethyl Ether with Tetrahydrofuran for Magnesium Compounds at the B3LYP/6-31+G* Level[a]

$Z\cdot nEt_2O + nTHF \rightarrow Z\cdot nTHF + nEt_2O$

Z	Δ*E*		Δ*H*		Δ*G*	
	n = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2
$MgCl_2$	−3.9	−8.7	−3.9	−8.8	−4.2	−8.3
$MgBr_2$	−4.1	−9.2	−4.1	−9.1	−4.8	−9.6
MeMgCl	−3.8	−8.5	−3.8	−8.4	−3.7	−7.8
MeMgBr	−4.0	−8.7	−3.9	−8.6	−4.5	−8.5
EtMgCl	−3.8	−8.3	−3.8	−8.3	−3.8	−8.4
EtMgBr	−4.0	−8.6	−4.0	−8.5	−5.0	−9.0
PhMgCl	−4.0	−9.0	−4.0	−9.0	−3.4	−9.0
PhMgBr	−4.1	−10.2	−4.2	−10.0	−3.5	−10.6
Me_2Mg	−3.7	−8.2	−3.7	−8.2	−3.7	−7.8
Et_2Mg	−3.9	−8.7	−3.9	−8.7	−3.7	−8.3
Ph_2Mg	−3.8	−9.2	−3.8	−9.2	−3.3	−9.1

$Z\cdot 2Et_2O + nTHF \rightarrow Z\cdot nTHF + 2Et_2O$

Z	Δ*E*		Δ*H*		Δ*G*	
	n = 3		*n* = 3		*n* = 3	
$MgCl_2$	−14.0		−13.6		−1.3	
$MgBr_2$	−13.3		−12.9		−0.7	
	cis, *n* = 4	*trans*, *n* = 4	*cis*, *n* = 4	*trans*, *n* = 4	*cis*, *n* = 4	*trans*, *n* = 4
$MgCl_2$	−8.3	−17.6	−7.9	−16.7	18.2	7.4
$MgBr_2$	−7.6	−16.1	−7.1	−15.6	19.1	11.2

[a] All values are in kcal/mol and include BSSE corrections.

TABLE 5: Energies (Δ*E*, contains zero-point vibrational energy (ZPVE) correction), Enthalpies (Δ*H*), and Gibbs Energies (Δ*G*) for the Schlenk Equilibria of Grignard Reagents in the Gas Phase and in Et_2O and THF Solutions at the B3LYP/6-31+G* Level[a]

	Δ*E*	Δ*H*	Δ*G*
$2RMgX \rightleftharpoons R_2Mg + MgX_2$			
MeMgCl	5.35	5.66	5.19
MeMgBr	5.25	5.72	4.81
EtMgCl	5.89	6.24	6.50
EtMgBr	6.14	6.55	6.48
PhMgCl	3.68	4.01	4.38
PhMgBr	6.19	6.64	6.62
$2(RMgX\cdot Et_2O) \rightleftharpoons R_2Mg\cdot Et_2O + MgX_2\cdot Et_2O$			
MeMgCl	4.00	3.97	4.75
MeMgBr	3.69	3.84	3.41
EtMgCl	4.32	4.29	5.08
EtMgBr	4.66	4.73	4.57
PhMgCl	1.91	1.83	3.06
PhMgBr	3.25	3.43	2.57
$2(RMgX\cdot 2Et_2O) \rightleftharpoons R_2Mg\cdot 2Et_2O + MgX_2\cdot 2Et_2O$			
MeMgCl	3.34	3.30	5.52
MeMgBr	3.07	3.20	2.70
EtMgCl	4.11	4.04	5.18
EtMgBr	4.65	4.59	4.96
PhMgCl	2.47	2.59	1.85
PhMgBr	2.22	2.61	1.09
$2(RMgX\cdot THF) \rightleftharpoons R_2Mg\cdot THF + MgX_2\cdot THF$			
MeMgCl	3.99	3.99	4.27
MeMgBr	3.74	3.80	3.95
EtMgCl	4.20	4.16	4.87
EtMgBr	4.72	4.69	6.05
PhMgCl	2.17	2.17	2.40
PhMgBr	3.53	3.99	1.55
$2(RMgX\cdot 2THF) \rightleftharpoons R_2Mg\cdot 2THF + MgX_2\cdot 2THF$			
MeMgCl	3.29	3.18	4.96
MeMgBr	2.97	3.07	2.31
EtMgCl	3.35	3.18	5.41
EtMgBr	3.98	3.79	4.97
PhMgCl	2.53	2.60	2.36
PhMgBr	4.18	4.28	3.64
$2(RMgX\cdot 2THF) + THF \rightleftharpoons R_2Mg\cdot 2THF + MgX_2\cdot 3THF$			
MeMgCl	−1.92, −3.23^b	−1.68, −3.00^b	11.94, 10.63^b
MeMgBr	−1.13, −6.17^b	−0.75, −5.79^b	11.22, 6.19^b
EtMgCl	−1.85, −3.20^b	−1.68, −3.03^b	12.39, 11.04^b
EtMgBr	−0.12, −5.40^b	−0.03, −5.31^b	13.87, 8.59^b
PhMgCl	−2.68, −3.99^b	−2.26, −3.57^b	9.34, 8.03^b
PhMgBr	0.08, −4.93^b	0.46, −4.55^b	12.55, 7.54^b
$2(RMgX\cdot 2THF) + 2THF \rightleftharpoons R_2Mg\cdot 2THF + \textit{cis}\ MgX_2\cdot 4THF$			
MeMgCl	3.69, 1.68^b	4.06, 2.04^b	31.49, 29.48^b
MeMgBr	4.60, −4.71^b	5.07, −4.24^b	31.03, 21.72^b
EtMgCl	3.76, 1.71^b	4.05, 2.01^b	31.94, 29.89^b
EtMgBr	5.62, −3.95^b	5.80, −3.76^b	33.69, 24.12^b
PhMgCl	2.93, 0.93^b	3.48, 1.47^b	28.89, 26.88^b
PhMgBr	5.82, −3.47^b	6.28, −3.01^b	32.36, 23.07^b
$2(RMgX\cdot 2THF) + 2THF \rightleftharpoons R_2Mg\cdot 2THF + \textit{trans}\ MgX_2\cdot 4THF$			
MeMgCl	−5.54, −8.27^b	−4.75, −7.47^b	20.66, 17.93^b
MeMgBr	−3.90, −21.99^b	−3.45, −21.54^b	23.19, 5.10^b
EtMgCl	−5.48, −8.24^b	−4.75, −7.51^b	21.10, 18.35^b
EtMgBr	−2.89, −21.23^b	−2.72, −21.06^b	25.85, 7.51^b
PhMgCl	−6.30, −9.02^b	−5.33, −8.04^b	18.06, 15.34^b
PhMgBr	−2.68, −20.75^b	−2.23, −20.30^b	24.52, 6.45^b

[a] All values are in kcal/mol and include BSSE corrections if not stated otherwise. [b] Values without BSSE corrections.

equatorial Mg−O bond in the $MgX_2\cdot 3THF$ complexes, but the situation is inverse in the case of cis $MgX_2\cdot 4THF$ complexes; the axial Mg−O bonds are shorter than the equatorial Mg−O bonds. The Mg−O bonds in the trans $MgX_2\cdot 4THF$ complexes are shorter than the axial and longer than the equatorial Mg−O bonds in the $MgX_2\cdot 3THF$ complexes.

3.2. Solvation Energies for Magnesium Compounds. The solvation energies of studied species with diethyl ether and tetrahydrofuran molecules were calculated from eqs 7 and 8, where Z is MgX_2, RMgX, and R_2Mg, and *n* is the number of

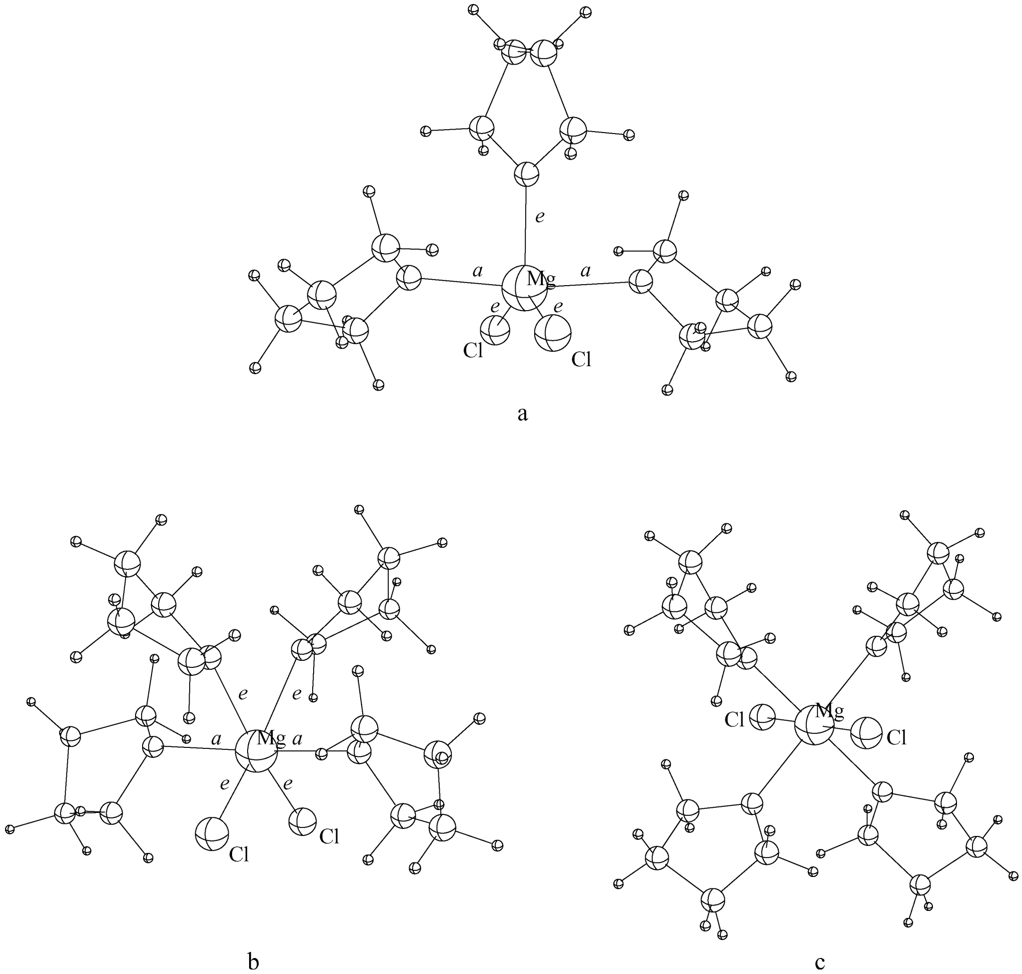

Figure 2. Optimized (at B3LYP/6-31+G* level of theory) structures of tris-tetrahydrofuranate and tetrakis-tetrahydrofuranate complexes of magnesium halide: (a) $MgCl_2 \cdot 3THF$, (b) cis $MgCl_2 \cdot 4THF$, and (c) trans $MgCl_2 \cdot 4THF$.

solvent molecules.

$$Z + nEt_2O \rightarrow Z \cdot nEt_2O \quad (n = 1-2) \tag{7}$$

$$Z + nTHF \rightarrow Z \cdot nTHF \quad (n = 1-4) \tag{8}$$

The results are given in Tables 2 and 3. The solvation enthalpies are exothermic for all the studied species. The solvent stabilization (with both one, ΔH_1, and two solvent molecules, ΔH_2) is largest for the magnesium halides, MgX_2, ($\Delta H_1 = -17.9$ to -21.6 kcal/mol, $\Delta H_2 = -29.8$ to -34.9 kcal/mol in Et_2O solution, and $\Delta H_1 = -21.9$ to -25.5 kcal/mol, $\Delta H_2 = -39.0$ to -43.7 kcal/mol in THF solution) and least for the diorganylmagnesium compounds, R_2Mg, ($\Delta H_1 = -9.2$ to -12.5 kcal/mol, $\Delta H_2 = -13.0$ to -18.6 kcal/mol in Et_2O solution, and $\Delta H_1 = -13.1$ to -16.3 kcal/mol, $\Delta H_2 = -22.0$ to -27.8 kcal/mol in THF solution) with intermediate values for the organomagnesium halides, RMgX, ($\Delta H_1 = -12.6$ to -15.9 kcal/mol, $\Delta H_2 = -20.4$ to -26.1 kcal/mol in Et_2O solution, and $\Delta H_1 = -16.5$ to -20.0 kcal/mol, $\Delta H_2 = -29.0$ to -35.1 kcal/mol in THF solution). The phenyl derivatives have larger solvation energies compared to the alkyl derivatives, which are sterically the most unfavorable. There is hardly any difference in solvation energies between compounds carrying Me or Et groups, but the chlorine-containing compounds are somewhat more strongly solvated than the corresponding bromine-containing compounds because of the more electronegative and smaller chlorine atom. The addition of the third THF molecule to $MgCl_2$ and $MgBr_2$ stabilizes the formed complexes only by 4.9 and 3.8 kcal/mol, respectively. The fourth THF molecule can have either a stabilizing or destabilizing effect on the energy of solvated complex, depending on the geometry of the complex. Cis $MgX_2 \cdot 4THF$ complexes are by 5.7 to 5.8 kcal/mol less stable than $MgX_2 \cdot 3THF$ + THF and by 0.9 to 2.0 kcal/mol less stable than $MgX_2 \cdot 2THF$ + 2THF, while trans $MgX_2 \cdot 4THF$ complexes are by 2.7 to 3.1 kcal/mol more stable than $MgX_2 \cdot 3THF$ + THF and by 6.5 to 7.9 kcal/mol more stable than $MgX_2 \cdot 2THF$ + 2THF.

THF, the stronger base, forms somewhat stronger Lewis acid−base complexes with studied magnesium compounds than does Et_2O. This becomes evident from the energies of displacement of Et_2O with THF for magnesium compounds (Table 4) expressed by eq 9.

$$Z \cdot nEt_2O + nTHF \rightarrow Z \cdot nTHF + nEt_2O \tag{9}$$

All displacement reactions are exothermic, indicating that the magnesium atom of each species prefers THF to Et_2O. The obtained energies of displacement are similar, $\Delta H_1 = -3.7$ to -4.2 kcal/mol, $\Delta H_2 = -8.2$ to -10.0 kcal/mol, respectively. The displacement of two Et_2O molecules with three or four THF molecules in the disolvated Et_2O complexes of MgX_2 is -12.9 to -13.6 kcal/mol (ΔH_3) and -7.1 to -7.9 kcal/mol in the case of cis complexes and -15.6 to -16.7 kcal/mol in the case of trans complexes (ΔH_4), respectively. The difference in energies between bromine-containing and chlorine-containing compounds is negligible, $\Delta\Delta H_1 = 0.1$ to 0.2 kcal/mol, $\Delta\Delta H_2 = 0.2$ to 1.0 kcal/mol, $\Delta\Delta H_3 = 0.7$ kcal/mol, and $\Delta\Delta H_4 = 0.8$ to 1.1 kcal/

TABLE 6: Collected Experimental Data for the Schlenk Equilibrium $2RMgX \rightleftharpoons R_2Mg + MgX_2$ at 298 K

Grignard reagent	solvent	ΔH (kcal/mol)	ΔF or ΔG (kcal/mol)	$1/K_s$	analysis method	ref
MeMgCl	THF			1.0 ± 0.72	NMR	7b
				4.5	IR	10
MeMgBr	Et_2O			320	calorimetric	8c
				450	kinetic + UV	12a,b
	THF			4.0 ± 2.6	NMR	7b
				3,5	IR	10
EtMgCl	THF	−3.80	1.010	5.52	calorimetric	9
EtMgBr	Et_2O	3.74	3.66	480	calorimetic	8a,b
	THF	−6.10	0.965	5.09	calorimetric	9
PhMgCl	THF	−2.72	0.300	1.66	calorimetric	9
PhMgBr	Et_2O	2.02	2.37	55−62	calorimetric	8b
	THF	−2.82	0.787	3.77	calorimetric	9
		-3.2 ± 0.5		4.0 ± 0.8	NMR	7a,c
		−4.47		7.46	NMR	7d
EtMgBr	dimethoxyethane			2.2 ± 0.3	polarographic	11
PhMgBr	dimethoxyethane			6.1 ± 0.3	polarographic	11

mol relative to bromine compounds, respectively. The experimental heats (ΔH) of displacement of Et_2O with THF are −19.1 kcal/mol for $MgBr_2$, −7.0 kcal/mol for EtMgBr, and −4.6 kcal/mol for Et_2Mg.[9] These data indicate that the degree of preference of THF over Et_2O is far greater for $MgBr_2$ than for EtMgBr or Et_2Mg. The best correspondence between the calculated and the above-mentioned experimental heats is found for trans $MgBr_2 \cdot 4THF$ ($\Delta H_{calc} = -15.6$ kcal/mol), for $EtMgBr \cdot 2THF$ ($\Delta H_{calc} = -8.5$ kcal/mol), and for $Et_2Mg \cdot THF$ ($\Delta H_{calc} = -3.9$ kcal/mol).

3.3. The Schlenk Equilibrium. The calculated energies for the Schlenk equilibria of monomeric Grignard reagents in the gas phase and in Et_2O and THF solutions are given in Table 5. The collected experimental data are listed in Table 6 for comparison.

The Schlenk equilibrium lies in favor of alkyl- and arylmagnesium halides in the gas phase according to our B3LYP/6-31+G* calculations; ΔH ranges from 4.01 to 6.64 kcal/mol. The solvation by diethyl ether has a quite strong influence on the equilibrium, decreasing the endothermicity of disproportionation reactions. The addition of the first Et_2O molecule has a stronger effect: disproportionation of monosolvated systems becomes by 1.69 to 3.21 kcal/mol less endothermic, and the addition of the second solvent molecule has a small 0.14 to 0.82 kcal/mol additional effect, except for PhMgCl where the second Et_2O molecule increases the endothermicity by 0.76 kcal/mol. The effect of solvation is the strongest in the case of PhMgBr, giving a value of $\Delta\Delta H_2 = \Delta H_{gas} - \Delta H_2 = 4.03$ kcal/mol; in the case of another species it ranges from 1.42 kcal/mol for PhMgCl to 2.52 kcal/mol for EtMgBr. Comparison of experimental and calculated energies for the disolvated systems indicates that most values obtained by calculations are somewhat bigger, e.g., $\Delta\Delta H_{calc(2)-exp}$ is 0.85 kcal/mol for EtMgBr, 0.59 kcal/mol for PhMgBr, and $\Delta\Delta G_{calc(2)-exp}$ is 1.30 kcal/mol for EtMgBr, but $\Delta\Delta G_{exp-calc(2)}$ is 1.28 kcal/mol for PhMgBr. The calculated values of ΔG for the monosolvated systems seem to be much more consistent with the experimental data for real solutions, $\Delta\Delta G_{calc(1)-exp}$ is 0.91 kcal/mol for EtMgBr and 0.20 kcal/mol for PhMgBr. However, the tendency that the predominant species in Et_2O is RMgX is still in agreement with experiment. We cannot ignore the fact that magnesium compounds exist as aggregates in real diethyl ether solution. The dimerization processes were calculated by Bock et al. in Me_2O[15] and by Lammertsma et al. in Et_2O.[17] As the Schlenk equilibrium is only slightly influenced by the association of Grignard reagents[17] and the dimerization energies decrease in the order $[MgX_2] > [RMgX] > [R_2Mg]$ (Cl > Br),[15,17] our calculations are limited to monomers.

The Schlenk equilibrium is shifted toward RMgX also in the case of solvation with one and two THF molecules according to our DFT calculations. From the experimental data it appears that the direction of reaction in THF shifts in favor of $R_2Mg + MgX_2$. It has been suggested that the difference in the Schlenk equilibrium between Et_2O and THF results from the increased coordination number of magnesium halide in THF (see section 3.1. in the current paper). Our computational results using the energies of $MgX_2 \cdot 3THF$ for the calculations of the disproportionation reactions support this argument. The correlation between the calculated values of ΔH without BSSE corrections and the corresponding experimental values is rather good, $\Delta\Delta H_{exp-calc(3)}$ is 0.77 kcal/mol for EtMgCl, 0.79 kcal/mol for EtMgBr, and $\Delta\Delta H_{calc(3)-exp}$ is 0.85 kcal/mol for PhMgCl and 0.08 to 1.73 kcal/mol for PhMgBr. The tendency that the alkyl- and arylmagnesium bromides are much more strongly disproportionated than the chlorides is also in agreement with experiment. It also becomes evident from the calculations using the energies of cis $MgX_2 \cdot 4THF$ without BSSE corrections, but the extent of disproportionation is smaller in the case of bromine compounds and the equilibrium is shifted toward the formation of organomagnesium halides in the case of chloride compounds. The results using the energies of trans $MgX_2 \cdot 4THF$ are more reasonable with BSSE corrections. The extent of disproportionation is somewhat more pronounced in the case of chloride compounds, which is not consistent with experimental data.

It seems that the used method of BSSE corrections is mostly not justified in the cases when $n = 3$ and 4, but it works well when $n = 1$ and 2. Such behavior can be attributed to the fact that the counterpoise correction seems to overestimate the magnitude of BSSE, especially for higher aggregates.

It should be noted that for the di-, tri-, and tetrasolvated complexes the values of ΔG differ considerably from the ΔE and ΔH, having even some positive values. It seems to be a fault of the used thermochemical analysis method, which treats all vibrational modes other than the free rotations and translations of molecule or complex as harmonic vibrations. For molecules having hindered internal rotations, this can produce errors in the energy and heat capacity at room temperatures and can have a significant effect on the entropy. Thus, the obtained values of ΔG are not reliable, especially in the case of solvation Gibbs energies and Gibbs energies for the Schlenk equilibrium using the corresponding total energies of tris- and tetrakis-tetrahydrofuranate complexes of magnesium halides. Therefore, no equilibrium constants for the disproportionation reactions were calculated.

4. Conclusions

The most important factor affecting the position of the Schlenk equilibrium is solvent. From the experimental data it appears that the predominant species is alkyl- or arylmagnesium halide, RMgX, in diethyl ether solution, and the disproportionation products, $R_2Mg + MgX_2$, are favored in tetrahydrofuran solution. The magnesium atom in RMgX, R_2Mg, and MgX_2 compounds can coordinate with two molecules of solvent in Et_2O in addition to the two covalent bonds. The difference in the Schlenk equilibrium between Et_2O and THF can be due to the increased coordination number of magnesium halide in THF, e.g., $MgX_2 \cdot n$THF ($n \geq 3$).

The tricoordinated magnesium is essentially planar in the monosolvated species, while the tetracoordinated magnesium forms with its ligands a deformed tetrahedron in the disolvated species. The tris-tetrahydrofuranate complex of magnesium halide is a deformed trigonal bipyramid, and both the tetrakis-tetrahydrofuranate complexes of magnesium halide, *cis*-dihalotetrakis(tetrahydrofurano)magnesium(II) and *trans*-dihalotetrakis(tetrahydrofurano)magnesium(II), are deformed octahedrons.

The solvation enthalpies are exothermic for all the studied magnesium compounds: RMgX, R_2Mg, and MgX_2 (R = Me, Et, Ph and X = Cl, Br). According to our DFT B3LYP/6-31+G* calculations the stabilization due to interaction with solvent molecules decreases in the order $MgX_2 > RMgX > R_2Mg$ and among the groups Ph > Me > Et and Cl > Br. THF, the stronger base, forms somewhat stronger Lewis acid−base complexes with studied species than does Et_2O.

Disproportionation reactions are slightly endothermic, favoring the organomagnesium halides in Et_2O solution. The Schlenk equilibrium is shifted toward the formation of the disproportionation products both in the case of tris-tetrahydrofuranate complex of MgX_2 and *trans*-tetrakis-tetrahydrofuranate complex of MgX_2, according to our calculations. Thus, magnesium halide is able to coordinate with up to four THF molecules, assuming that *trans*-dihalotetrakis(tetrahydrofurano)magnesium(II) forms. The formation of *cis*-dihalotetrakis(tetrahydrofurano)magnesium(II) is energetically even less favorable than the corresponding disolvated complexes.

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Supporting Information Available: Optimized structures of mono- and disolvated phenylmagnesium chloride and diphenylmagnesium. This material is available free of charge via the Intenet at http://pubs.acs.org.

References and Notes

(1) Grignard, V. *C. R. Hebd. Seances Acad. Sci.* **1900**, *130*, 1322.

(2) Schlenk, W.; Schlenk, W., Jr. *Chem. Ber.* **1929**, *62*, 920.

(3) Cannon, K. S.; Krow, G. R. In *Handbook of Grignard Reagents* and references therein; Silverman, G. S., Rakita, P. E., Eds.; Marcel Dekker: New York, 1996.

(4) Lindsell, W. E. In *Comprehensive Organometallic Chemistry* and references therein; Wilkinson, G., Ed.; Pergamon Press: Elmsford, NY, 1982; Vol. 1, Chapter 4.

(5) Walker, F. W.; Ashby, E. C. *J. Am. Chem. Soc.* **1969**, *91*, 3845.

(6) (a) Ashby, E. C.; Smith, M. B. *J. Am. Chem. Soc.* **1964**, *86*, 4363. (b) Ashby, E. C.; Becker, W. E. *J. Am. Chem. Soc.* **1963**, *85*, 118.

(7) (a) Evans, D. F.; Fazakerley, V. *J. Chem. Soc. A* **1971**, 184. (b) Parris, G. E.; Ashby, E. C. *J. Am. Chem. Soc.* **1971**, *93*, 1206. (c) Evans, D. F.; Fazakerley, V. *Chem. Commun.* **1968**, 974. (d) Markies, P. R.; Altink, R. M.; Villena, A.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1991**, *402*, 289.

(8) (a) Smith, M. B.; Becker, W. E. *Tetrahedron Lett.* **1965**, *43*, 3843. (b) Smith, M. B.; Becker, W. E. *Tetrahedron* **1966**, *22*, 3027. (c) Holm, T. *Acta Chem. Scand.* **1969**, *23*, 579.

(9) Smith, M. B.; Becker, W. E. *Tetrahedron* **1967**, *23*, 4215.

(10) Salinger, R. M.; Mosher, H. S. *J. Am. Chem. Soc.* **1964**, *86*, 1782.

(11) Psarras, T.; Dessy, R. E. *J. Am. Chem. Soc.* **1966**, *88*, 5132.

(12) (a) Ashby, E. C.; Laemmle, J.; Neumann, H. M. *J. Am. Chem. Soc.* **1971**, *93*, 4601. (b) Ashby, E. C.; Laemmle, J.; Neumann, H. M. *J. Am. Chem. Soc.* **1972**, *94*, 5421.

(13) Ohkubo, K.; Watanabe, F. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2867.

(14) Kato, H.; Tsuruya, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1001.

(15) Axten, J.; Troy, J.; Jiang, P.; Trachtman, M.; Bock, C. W. *Struct. Chem.* **1994**, *5*, 99.

(16) Tammiku, J.; Burk, P.; Tuulmets, A. *J. Phys. Chem. A* **2001**, *105*, 8554.

(17) (a) Ehlers, A. W.; van Klink, G. P. M.; van Eis, M. J.; Bickelhaupt, F.; Nederkoorn, P. H. J.; Lammertsma, K. *J. Mol. Model.* **2000**, *6*, 186. (b) Yamazaki, S.; Yamabe, S. *J. Org. Chem.* **2002**, *67*, 9346.

(18) (a) Guggenberger, L. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1964**, *86*, 5344. (b) Guggenberger, L. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 5375.

(19) Stucky, G.; Rundle, R. E. *J. Am. Chem. Soc.* **1964**, *86*, 4825.

(20) Schibilla, H.; Le Bihan, M.-T. *Acta Crystallogr.* **1967**, *23*, 332.

(21) Schröder, F. Dissertation, Institut für Anorganische Chemie der Technischen Hochschule, Braunschweig, Germany, 1965.

(22) (a) Schröder, F.; Spandau, H. *Naturwiss.* **1966**, *53*, 360. (b) Perucaud, M.; Ducom, J.; Vallino, M. *Compt. Rend.* **1967**, *264*, 571.

(23) *Gaussian 98*, revision A7; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1998.

(24) Van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H. *Chem. Rev.* **1994**, *94*, 1873.