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# Structural studies of organometallic compounds in solution

## III *. A large angle scattering (LAXS) study of organomagnesium iodides in diethyl ether

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### Abstract

Structures of methyl-, ethyl- and phenyl-magnesium iodides have been determined in diethyl ether solution by the large angle X-ray scattering (LAXS) technique. Solutions in the concentration range 0.9–2.7 *M* have been studied. The Grignard reagents are present as solvated monomeric and dimeric species. Magnesium coordinates an iodide ion, an alkyl or aryl group, and four diethyl ether molecules octahedrally in the monomeric complex. In the dimeric complex each magnesium is octahedrally coordinated by two bridging iodide ions, an alkyl or aryl group, and three solvent molecules. The distribution of monomeric and dimeric species in the different solutions is given by a dimerisation constant, $K_{di} = [(RMgX)_2][RMgX]^{-2}$, which is in the range 0.2–0.8 $M^{-1}$. The Mg–I bond distance is between 2.74 and 2.81 Å.

## Introduction

Grignard compounds have been of much interest to organic chemists for almost a century since very valuable transformations, including carbon–carbon bond formation, can be achieved with organomagnesium compounds as intermediates [1]. In recent years organomagnesium compounds have also been shown to be important intermediates in applications of organotransition metal chemistry synthesis [2,3]. To understand the mechanism of the Grignard reactions, often performed in diethyl ether, structural information on the reacting species in this solvent is desirable. The actual structure of Grignard reagents in solution has been a matter of controversy for many years [4].

To our knowledge no crystallographic studies of organomagnesium iodides have been published. In the solid phenylmagnesium bromide dietherate one bromide ion,

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* For Part II see ref. 41.

one phenyl group, and two diethyl ether molecules are tetrahedrally coordinated to magnesium in a monomeric complex, and the Mg–Br bond distance is 2.44 Å [5]. In the corresponding ethyl compound [6], which is also monomeric and tetrahedral, the Mg–Br distance is 2.48 Å. For tetrahydrofuran, THF, solvates an octahedral arrangement around $MgBr_2$ has been reported [7–9]. In solid $MeMgBr(THF)_2$ the magnesium is five-coordinate [10] at the centre of a trigonal bipyramid. IR and Raman spectra have been recorded of diethyl ether and THF solvated methylmagnesium iodide and bromide for both solids and solution [11]. The basic structures of the compounds in the solid state seem to be similar. However, two crystalline forms of $MeMgBr(Et_2O)_2$ were identified, differing in the conformations of the coordinated diethyl ether molecules. Raman studies of Grignard compounds in diethyl ether solution have shown that the dominant species in the concentration range 0.5–4 *M* is disolvated monomers [11]. The IR spectra of $Me_2Mg$ and MeMgBr in THF solution are significantly different. The THF solution of MeMgBr is best represented as an equilibrium mixture of $Me_2Mg$, $MgX_2$ and MeMgX, MeMgX being the predominant species for the bromide and chloride. Similar assumptions could not be made for the diethyl ether solutions since the spectra were inconclusive, except in the case of the phenylmagnesium iodide solution, in which monomeric PhMgI is the dominant species [12].

The Grignard solutions have also been studied by several other physical chemistry techniques, namely, ebullioscopy, conductivity, electrolysis, and NMR. Ebullioscopic measurements in tetrahydrofuran showed that the Grignard compounds are monomeric in the concentration range studied, 0.1–2 *M* [13]. It was further indicated that in diethyl ether the degree of association of organomagnesium bromides, in general, increased with increasing concentration. The conductivity in diethyl ether solutions has been determined at various temperatures. Of the solutions studied, those of phenylmagnesium bromide showed the lowest conductivity [14]. The conductivity increased with increasing concentration in the range 0.5–2.0 *M*. For all the solutions except 2.0 *M* phenylmagnesium bromide the conductivity increased with decreasing temperature. The apparent molecular weights in solution have been determined by a variety of techniques. The deductions that can be made from such measurements do not give any information on the degree of solvation or on how to Grignard compounds are associated. The $^{25}$Mg NMR spectra of EtMgBr in THF showed three distinguishable species at 37 °C: $Et_2Mg$, $MgBr_2$ and EtMgBr. The broader signal of $Et_2Mg$ is superimposed on that of EtMgBr, but signals from $MgBr_2$ and EtMgBr are resolved. The appearance of these NMR spectra depends on the concentrations and temperature. For EtMgBr two signals can be resolved at fairly high temperatures whereas MeMgBr already displays an average signal at 27 °C since the equilibrium constant is larger than that for EtMgBr [15]. For MeMgX in diethyl ether $^1$H NMR spectroscopy has been largely unsuccessful in distinguishing between various species. At low temperatures MeMgBr can be distinguished from $Me_2Mg$; at −100 °C two signals are observed [16].

Even though it is nearly 90 years since Grignard first synthesised this type of compounds [17], their structures, kinetics and reaction mechanisms are still not fully understood. The X-ray scattering technique has been applied to other systems to solve structural problems [18]. We here report the results of a large angle X-ray scattering (LAXS) study of a number of Grignard reagents in diethyl ether solution. Organomagnesium iodide compounds were used to maximise the scattering power of the magnesium halide entity. In order to get reliable results from LAXS measurements, concentrated solutions are required. Solutions in the concentration range 0.9–2.7 *M* were used. To determine the concentration dependence of the composition of the solutions, various concentrations of various iodides were used. All measurements were carried out at room temperature.

## Experimental

All glass equipment and syringe needles had been dried in an oven and all operations were carried out under dry, oxygen-free nitrogen or argon.

### *Solvents*

Anhydrous diethyl ether and tetrahydrofuran purchased from Aldrich in Sure/Seal$^{TM}$ bottles were used. The solvents were transferred with hypodermic syringes.

### *Reagents*

Iodomethane was used as supplied by Merck, iodoethane by Janssen, and iodobenzene by Fluka. Grignard reagent grade magnesium turnings (Merck) were used.

### *Preparation of organomagnesium iodide solutions*

The Grignard compounds were prepared in 250-ml, round-bottomed, three-necked flasks. The weighed amount of magnesium turnings and a magnetic stirring bar were placed in the flask which was fitted with an addition funnel and a reflux condenser. 10 ml of solvent was added to the flask and another 90 ml was added to the organic iodide in the addition funnel. The amount of organic iodide was adjusted to give the desired concentration of the Grignard solution. 5 ml of the halide mixture was added to the flask and the reaction started. In none of the cases was it necessary to add an initiator. The remaining iodide solution was added dropwise. The mixture was refluxed and stirred for an hour after all the halide had been added and was then left to settle. The solution was transferred to a Schlenk tube and filtered. All transfers from storage bottles to sample cells were carried out with hypodermic syringes.

### *Analyses*

All the organomagnesium solutions were analysed for magnesium by EDTA titration using Eriochrome Black T as indicator in aqueous solution.

The phenylmagnesium iodide solutions were analysed for PhMgI by adding dry ice and weighing the benzoic acid formed after hydrolysis, evaporation of the ether and thorough drying. $^1$H NMR spectra were recorded on a Varian XL-300 spectrometer in deuterochloroform for the phenylmagnesium iodide solutions before and after the scattering measurements to confirm that the composition of the solutions remained unchanged.

### *Data collection*

A large angle $\theta$–$\theta$ diffractometer of the Seifert GSD type with Mo-$K_\alpha$ radiation ($\lambda = 0.7107$ Å) was used to measure the scattered intensities from the free surface of

Table 1

Composition of the solutions studied

| Solution | $[Mg^{2+}]$ ($M$) | [Solvent] ($M$) | $\mu$ ($cm^{-1}$) |
|---|---|---|---|
| $CH_3MgI$ | 1.4 | 9.5 | 7.3 |
| | 2.7 | 9.2 | 13.3 |
| $C_2H_5MgI$ | 0.9 | 9.3 | 4.9 |
| | 2.7 | 7.6 | 13.4 |
| $C_6H_5MgI$ | 0.9 | 9.3 | 5.5 |
| | 1.5 | 8.5 | 8.2 |

the solutions [19]. A curved graphite or lithium fluoride monochromator was placed immediately before the scintillation counter. The solutions were kept in the previously described [20] cylindrical, thin-walled glass vessel in order to avoid evaporation and to keep out moisture and air. The container was half-filled. A correction function for the angle dependent absorption by the glass container was determined and applied as described elsewhere [20]. Scattered intensities were collected in the range $4 < \theta < 55°$ with steps of $s = 0.0335$ Å$^{-1}$, $s = 4\pi \sin\theta \lambda^{-1}$. The scattering angle is $2\theta$. An extrapolation of the intensity data for $\theta < 4°$ was necessary because of the upward liquid meniscus on the glass wall. The reproducibility was checked by repeated scans. 20000 counts were collected for $s < 10.2$ Å$^{-1}$ 8000 counts for $10.2 \leqslant s \leqslant 14.5$. The number of collected counts for $s > 10.2$ Å$^{-1}$ was decreased due to the very long counting time. The counting time for each sampling point was never less then 20 min.

### *Data treatment*

Experimental data were initially corrected for background scattering and polarisation effects [19]. Correction for multiple scattering was made because of the low absorption coefficients [21], Table 1. The corrected data were normalised to a stoichiometric volume containing one magnesium atom. The normalisation factor, $K$, used in the data analysis was derived by comparison of the measured and total independent scattering in the high-angle region, $s > 13$ Å$^{-1}$. $K$ calculated in this manner was then compared with $K$ calculated according to Krogh-Moe [22] and Norman [23].

Scattering factors, $f$, for the neutral atoms were used [24] except for H, for which the spherical form factors suggested by Stewart et al. were employed [25]. The contribution from anomalous dispersion, $\Delta f'$ and $\Delta f''$, was considered for all atoms [24]. Incoherent scattering factors [26–28], corrected for the Breit–Dirac effect [29,30], were used. The raw data were normal up to $s \approx 10$ Å$^{-1}$, where an unexpected decrease in the total intensity was observed. The structural information was, however, not affected by this decrease in intensity. The intensity function was straightened up by applying a smoothed correction function to the experimental data, in such a way that one Fourier transformation was enough to straighten up the entire experimental function, as is the usual case. All these corrections were taken into account when the reduced intensity function, $i(s)$, Fig. 1, and the differential radial distribution functions, $D(r) - 4\pi r^2\rho_0$, Fig. 2, were calculated using standard procedures [31,32]. Spurious peaks below 1.5 Å which could not be identified with interatomic distances in the solutions, were removed by a Fourier transformation procedure [33].

All calculations were made with the program KURVLR [34]. Least-squares refinements were carried out with the STEPLR program [35].

## Results

The studied Grignard compounds in diethyl ether solution seem to have the same basic structure. In the radial distribution functions (RDFs) there is a peak at about 2.8 Å corresponding to the Mg–I bond distance within the Grignard compound, and another peak at 1.5 Å matching the intramolecular distances in the diethyl ether molecule and in the alkyl or phenyl group, Fig. 2. The size of the Mg–I peak is somewhat larger than expected for a monomeric structure, but smaller than expected for a dimeric structure. There is also a marked shoulder at 3.9 Å which is assigned to an I–I distance in a dimer where the magnesium ions are six-coordinated, or to an I–C distance in tetrahedral monomeric or dimeric species. The intensity of this interaction corresponds well to $(n(\text{Mg–I}) - 1)/2$ I–I distances as expected for a dimeric structure. $n(\text{Mg–I})$ is the number of Mg–I distances. For dimeric species where magnesium is tetrahedrally coordinated, an I–I distance is expected at about 4.6 Å. A weak interaction is indeed found in the RDFs at 4.5 Å, but it corresponds poorly with the number of Mg–I distances. This interaction can instead be assigned to an intermolecular distance between the diethyl ether molecules. This is seen as a peak in the difference curve for the octahedral models in Fig. 2. The I–C distance in a tetrahedral model cannot fully compensate for the experimental interaction observed at 3.9 Å. This strongly indicates that both monomeric and dimeric Grignard species are present in the diethyl ether solutions studied, and that the magnesiums are octahedrally coordinated in the dimeric species. It is not possible from the present data to distinguish between tetrahedral and octahedral geometry of the monomeric species, since the I–O and I–C interactions have too weak scattering power to be seen as well-defined peaks or shoulders in the RDFs. We therefore chose to use octahedral monomeric and dimeric species in the final calculations.

Least-squares refinements were performed with both octahedral and tetrahedral models and with either only monomers or with mixtures of monomeric and dimeric species. It was only possible to refine the Mg–I distance, $d$, and its temperature factor, $b$, with a least-squares minimisation. All the other parameters were either obtained by curve-fitting using the KURVLR program [34], or were fixed at values estimated from previous studies [20,36]. The parameters for the diethyl ether molecule and the C–C distances in the alkyl and phenyl groups are the same for all the solutions. Substantially lower error-square sums and better curve fits were obtained for the model containing dimeric species. The Mg–C parameters were set to the following values: $d = 2.20$ Å, $b = 0.006$ Å$^2$, $n = 1.0$ for the octahedral complexes and $d = 2.15$ Å, $b = 0.006$ Å$^2$, $n = 1.0$ for the tetrahedral complexes. The following Mg–O parameters were used: $d = 2.15$ Å, $b = 0.008$ Å$^2$, $n = 5 - n(\text{Mg–I})$ for octahedral complexes and $d = 2.05$ Å, $b = 0.008$ Å$^2$, $n = 3 - n(\text{Mg–I})$ for tetrahedral complexes. The Mg–O and Mg–C parameters in the tetrahedral model are taken from the structure of $C_2H_5MgBr \cdot 2CH_3OCH_3$ [6]. For the octahedral

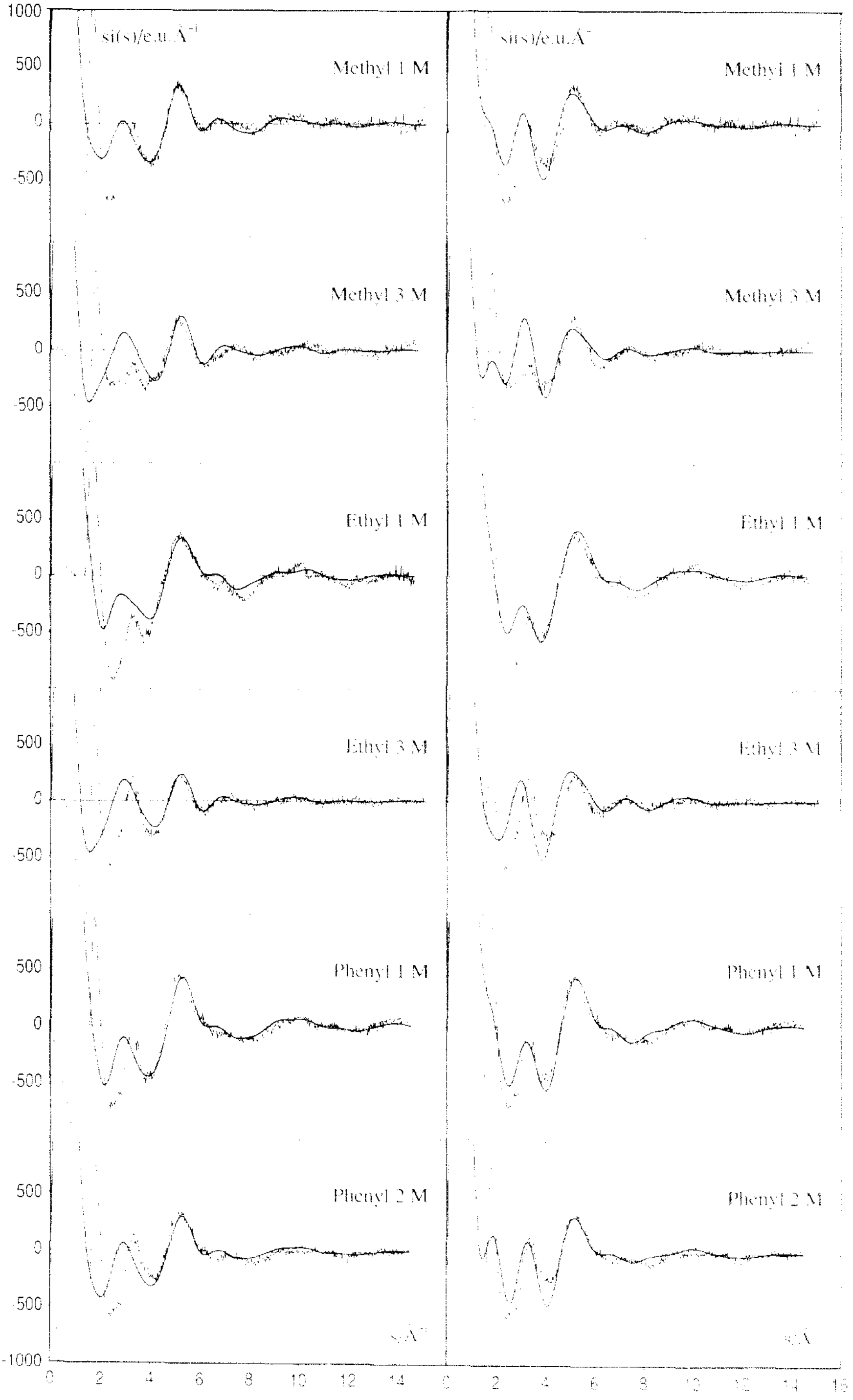


Fig. 1. Reduced intensities, $i(s)$, multiplied by $s$ vs $s$ for organomagnesium iodides in diethyl ether. Experimental values are represented by the thin lines and the values calculated from the final structure models in Table 2 by the thick lines. The models with octahedrally coordinated magnesium ions are shown to the left, and the corresponding models with tetrahedrally coordinated magnesium ions are shown to the right.

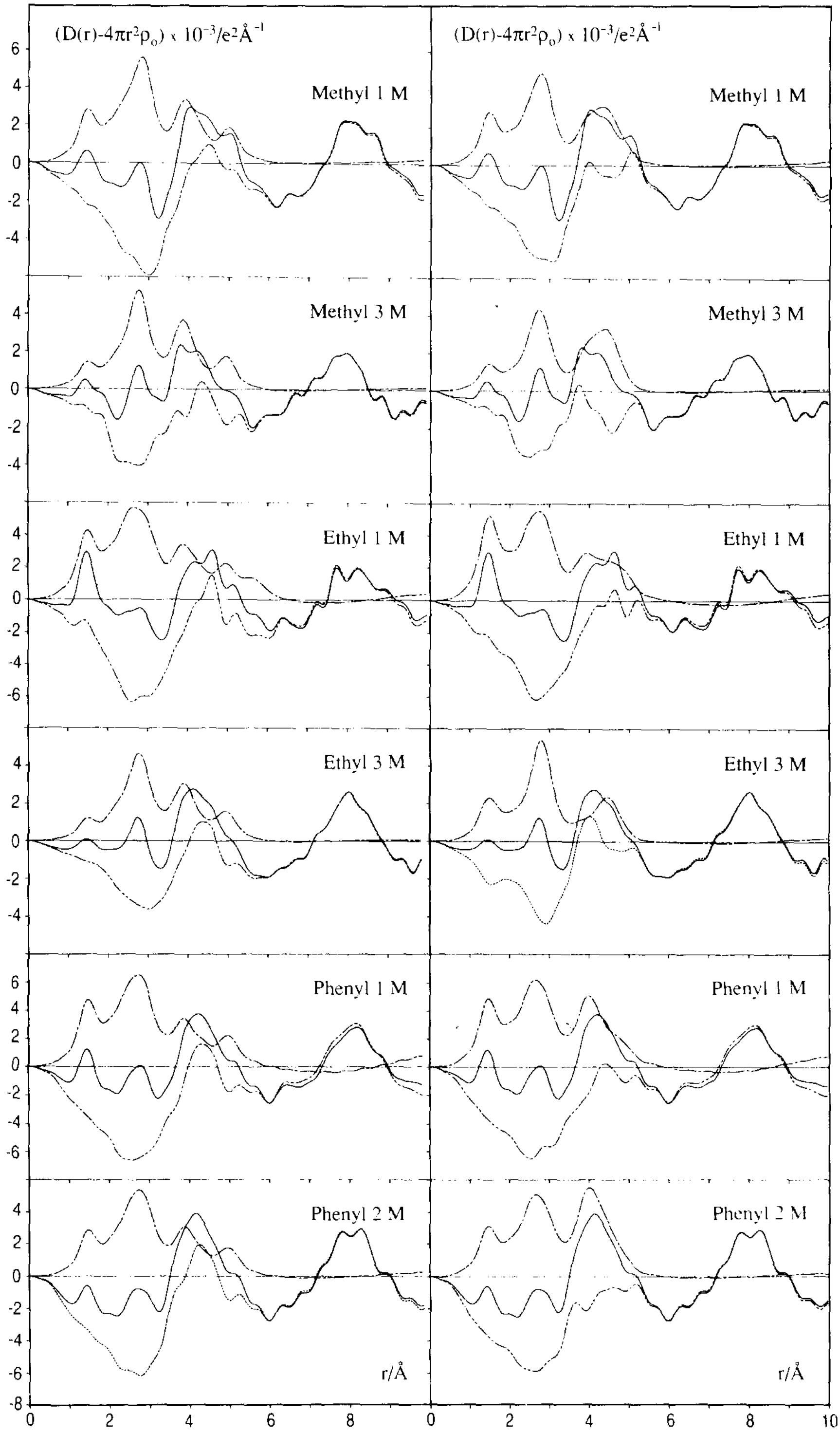


Fig. 2. The differential electronic radial distribution function, $D(r)-4\pi r^2\rho_0$, for organomagnesium iodides in diethyl ether solution, solid lines. The dashed lines represent the sum of the calculated peak shapes and the difference is drawn with double-dashed lines. The models with octahedrally coordinated magnesium ions are shown to the left, and the models with tetrahedrally coordinated magnesium ions are shown to the right.

Table 2

Interatomic distances, *d* (Å) temperature factor coefficient, *b* (Å$^2$) and the number of distances per magnesium atom, *n*, for the solutions investigated; errors derived from the least-squares refinements are given in parentheses

| Solution | Model | Conc. (*M*) | Dimerisation (%) | *d*(Mg–I) | *b*(Mg–I) | *n*(Mg–I) | *d*(I–I) | *b*(I–I) | *n*(I–I) | *d*(I–C) | *b*(I–C) | *n*(I–C) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3MgI$ | Oct. | 1.4 | 46 | 2.83(2) | 0.006(2) | 1.46 | 4.00 | 0.025 | 0.23 | 3.58 | 0.020 | 0.46 |
| $CH_3MgI$ | Tetr. | 1.4 | 46 | 2.84(2) | 0.007(2) | 1.46 | 4.63 | 0.025 | 0.23 | 4.10 | 0.020 | 0.46 |
| $CH_3MgI$ | Oct | 2.7 | 54 | 2.75(2) | 0.006(2) | 1.54 | 3.88 | 0.025 | 0.27 | 3.52 | 0.020 | 0.54 |
| $CH_3MgI$ | Tetr. | 2.7 | 54 | 2.77(2) | 0.007(2) | 1.54 | 4.52 | 0.025 | 0.27 | 4.03 | 0.020 | 0.54 |
| $C_2H_5MgI$ | Oct. | 0.9 | 30 | 2.81(2) | 0.009(3) | 1.30 | 3.97 | 0.025 | 0.15 | 3.57 | 0.020 | 0.30 |
| $C_2H_5MgI$ | Tetr. | 0.9 | 30 | 2.82(2) | 0.009(3) | 1.30 | 4.61 | 0.026 | 0.15 | 4.08 | 0.020 | 0.30 |
| $C_2H_5MgI$ | Oct. | 2.7 | 45 | 2.76(2) | 0.010(2) | 1.45 | 3.90 | 0.025 | 0.23 | 3.53 | 0.020 | 0.45 |
| $C_2H_5MgI$ | Tetr. | 2.7 | 45 | 2.83(2) | 0.009(2) | 1.45 | 4.62 | 0.025 | 0.23 | 4.09 | 0.020 | 0.45 |
| $C_6H_5MgI$ | Oct. | 0.9 | 25 | 2.80(2) | 0.009(2) | 1.25 | 3.93 | 0.025 | 0.13 | 3.53 | 0.020 | 0.25 |
| $C_6H_5MgI$ | Tetr. | 0.9 | 25 | 2.78(2) | 0.009(2) | 1.25 | 4.54 | 0.025 | 0.13 | 4.04 | 0.020 | 0.25 |
| $C_6H_5MgI$ | Oct. | 1.5 | 34 | 2.81(2) | 0.009(2) | 1.34 | 3.88 | 0.025 | 0.17 | 3.52 | 0.020 | 0.34 |
| $C_6H_5MgI$ | Tetr. | 1.5 | 34 | 2.82(2) | 0.009(2) | 1.34 | 4.49 | 0.025 | 0.17 | 4.02 | 0.020 | 0.34 |

Table 3

The estimated dimerisation constants $K_{di}$ ($M^{-1}$), of Grignard compounds in diethyl ether solution. The estimated error in $K_{di}$ is less than 50%

| System | $K_{di}$ |
|---|---|
| $CH_3MgI$ | 0.55 |
| $C_2H_5MgI$ | 0.23 |
| $C_6H_5MgI$ | 0.25 |

model the choice of 2.15 Å for the Mg–O distance is based on the Mg–O distance in the hydrated magnesium ion: 2.11 Å [37], and it can be assumed that this distance is slightly longer for the more weakly solvating diethyl ether molecule. The ionic radius of magnesium increases with about 0.14 Å when going from tetrahedral to octahedral configuration [38], but as it is assumed that the Mg–C bond is substantially stronger than the Mg–O solvate bonds, the Mg–C bond distance has been set to 2.20 Å. The I–I and I–C distances were calculated from the refined Mg–I bond distance, and the number of I–I, I–C and Mg–O distances were obtained by curve-fitting. The temperature factor coefficients for the I–I and I–C distances have been set to 0.025 and 0.020 Å$^2$, respectively. The parameters obtained from least-squares refinements and curve-fitting are summarised for the systems studied in Table 2.

These comparisons show that a model involving both monomeric and dimeric alkyl Grignard species where magnesium is octahedrally coordinated gives the best fit to the experimental data (see Figs. 1 and 2). For phenylmagnesium iodide, however, an equally good fit is obtained for a model with tetrahedrally coordinated magnesium (see Figs. 1 and 2).

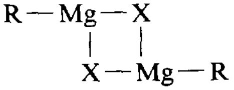
The degree of dimerisation was determined for each sample studied, by curve-fitting the number of I–I distances and a dimerisation constant, $K_{di} = [(RMgI)_2][RMgI]^{-2}$, was calculated. In the final calculations of the theoretical RDFs, the degree of dimerisation used was that obtained from the average of the dimerisation constants calculated for the various concentrations of a particular Grignard compound. The estimated dimerisation constants are given in Table 3.

## Discussion

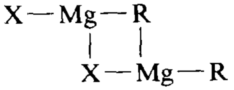
This study has shown that the Grignard reagents are present as both solvated monomeric and dimeric species. The degree of dimerisation is dependent on both the concentration and the R group, and is determined by the equilibrium 2 RMgX $\rightleftharpoons$ $(RMgX)_2$, which corresponds to the left hand side of an expanded Schlenk equilibrium [38]:

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

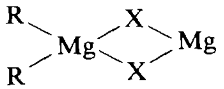
where $(RMgX)_2$ is either structure I or II and $R_2Mg \cdot MgX_2$ is represented by the structure in III. Note that solvent molecules are omitted.



(I)



(II)



(III)

This study supports the occurrence of dimerisation of Grignard compounds, and not the formation of $R_2Mg$ and $MgX_2$, in diethyl ether solution. If these two species were present it would not be possible to curve-fit the number of I–I distances with a dimerisation constant since the number of I–I distances per magnesium in $(RMgI)_2$ and $MgI_2$ are different, viz. 0.5 and 1.5, respectively. The dimerisation constants, $K_{di}$, are fairly small (Table 3), but the dimerisation cannot be neglected at any concentration, including very dilute solutions.

In the monomeric Grignard complexes magnesium most probably coordinates one iodide, one alkyl or aryl group and four diethyl ether molecules in an octahedral fashion (Fig. 5b, ref. 40). The experiments cannot rule out tetrahedral coordination around magnesium in the monomeric complexes, but they have shown that the dimeric species have octahedral configuration. It is therefore reasonable to believe that the monomeric species are also octahedral. In the dimeric structure one diethyl ether is replaced by a bridging iodide. A dimeric structure with one bridging iodide and one bridging R group, II, cannot be excluded from the structural results. This structure seems less likely though, for several reasons. Such a dimeric structure must have a dipole moment and would have low solubility in diethyl ether, which has a low dielectric constant. Bridging and terminal halides normally have different bond distances, which in LAXS studies would result in larger *b* factors than expected for a certain coordination geometry. *b* factors are normally around 0.010 $Å^2$ for metal–ligand and metal–solvate bond distances in an octahedral configuration [37]. This dimeric structure would imply that the tendency to act as bridging group would be the same for a halide ion as for an alkyl group, which seems unlikely. The dimeric structure $R_2Mg \cdot MgX_2$ (III), which has been suggested [4], also seems unlikely chemically. It cannot be excluded by our measurements but instead of an $R_2Mg \cdot MgX_2$ complex one would expect a statistical distribution of the halide and alkyl ligands between the two magnesiums.

The refinement of the data was very difficult but in the end the best fits were obtained with models having octahedral coordination around magnesium, at least in the dimeric species. In Fig. 5b, ref. 40, the tetrahedral models are also shown for comparison. Tetrahedral magnesium complexes seem to be present only when the solvent activity is very low, as in solids [5,6] or in extremely concentrated solutions [41].

These results do not exclude a trigonal bipyramidal structure around magnesium in diethyl ether solvated Grignard compounds either. A large number of structural studies of solvated metal complexes in solution have shown that hard metal ions, such as magnesium, tend to adopt the maximum coordination number, which is six for magnesium [37]. It is assumed that this is also the case for the Grignard reagents in diethyl ether solution, and that trigonal bipyramidal configurations are observed only when the solvent activity is low, as in solids [10].

Preliminary studies of n-pentylmagnesium iodide and 2,5-dimethyl-thienylmagnesium iodide give similar results, and also indicate that these findings can be extended to include at least certain electron-rich heteroaromatic Grignard reagents.

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## References

1 J. March, Advanced Organic Chemistry, 3rd ed., John Wiley & Sons, New York, 1985.
2 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, 2nd ed, University Science Books, Mill Valley, 1987, pp. 178 and 712.
3 S.G. Davies, Organotransition Metal Chemistry: Applications to Organic Synthesis, Pergamon Press, Oxford, 1982, p. 218.
4 For reviews see: E.C. Ashby, Bull. Soc. Chim. Fr., (1972) 2133; B.J. Wakefield, Organomet. Chem. Rev., 1 (1966) 131.
5 G.D. Stucky and R.E. Rundle, J. Am. Chem. Soc., 86 (1964) 4825.
6 L.J. Guggenberger and R.E. Rundle, J. Am. Chem. Soc., 90 (1968) 5375.
7 M-C. Pérucaud and M-T. Le Bihan, Acta Crystallogr., Sect. B, 24 (1968) 1502.
8 R. Sarma, F. Ramirez, B. Mckeever, Y.F. Chaw, J.F. Marecek, D. Nierman and T.M. McCaffrey, J. Am. Chem. Soc., 99 (1977) 5289.
9 F. Schröder and H. Spandau, Naturwissenschaften, 53 (1966) 360.
10 M. Vallino, J. Organomet. Chem., 20 (1969) 1.
11 J. Kress and A. Novak, J. Organomet. Chem., 99 (1975) 199.
12 R.M. Salinger and H.S. Mosher, J. Am. Chem. Soc., 86 (1964) 1782.
13 F.W. Walker and E.C. Ashby, J. Am. Chem. Soc., 91 (1969) 3845.
14 W.V. Evans and F.H. Lee, J. Am. Chem. Soc., 55 (1933) 1474.
15 R. Benn, H. Lehmkuhl, K. Mehler and A. Rufinska, Angew. Chem., Int. Ed. Engl., 23 (1984) 543.
16 G.E. Parris and E.C. Ashby, J. Am. Chem. Soc., 93 (1971) 1206.
17 V. Grignard, C. R. 130 (1900) 1322.
18 M. Magini, G. Licheri, G. Piccaluga, G. Paschina, G. Pinna (Eds.), X-ray Diffraction of Ions in Aqueous Solution: Hydration and Complex Formation, CRC Press Cleveland, OH, 1988.
19 G. Johansson, Acta, Chem. Scand., 20 (1966) 553.
20 I. Persson, M. Sandström, P.L. Goggin and A. Mosset, J. Chem. Soc., Dalton Trans. (1985) 1597.
21 B.E. Warren, X-ray Diffraction, Addison–Wesley, Reading, MA, 1969, Ch. 10.
22 J. Krogh-Moe, Acta Crystallogr., 9 (1956) 951.
23 N. Norman, Acta Crystallogr., 10 (1957) 370.
24 International Tables of Crystallography, Kynoch Press, Birmingham, UK, Vol. 3, 1968 and Vol. 4, 1974.
25 R.F. Stewart, E.R. Davidsson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
26 D.T. Cromer and J.B. Mann, J. Chem. Phys., 47 (1967) 1892.
27 D.T. Cromer, J. Chem. Phys., 50 (1969) 4857.
28 A.H. Compton and S.K. Allison, X-ray in Theory and Experiment, van Nostrand–Reinhold, New York, 1935.
29 G. Breit, Phys. Rev., 27 (1926) 362.
30 P.A.M. Dirac, Proc. R. Soc. London, 4 (1926) 195.
31 G. Johansson, Acta Chem. Scand., 25 (1971) 2787.
32 M. Sandström and G. Johansson, Acta Chem. Scand., Ser. A, 31 (1977) 132.
33 H.A. Levy, M.D. Danford and A.H. Narten, Data Collection and Evaluation with X-ray Diffractometer Designed for the Study of Liquid Structure, Report ORNL-3690, Oak Ridge National Laboratory, Oak Ridge, 1966.
34 G. Johansson and M. Sandström, Chem. Scr., 4 (1973) 195.
35 M. Molund and I. Persson, Chem. Scr., 25 (1985) 197.
36 S. Ahrland, E. Hansson, Å, Iverfeldt and I. Persson, Acta Chem. Scand., Ser. A, 35 (1981) 275.
37 R. Caminiti, G. Licheri, G. Piccaluga and G. Pinna, Chem. Phys. Lett., 61 (1979) 45; idem, J. Appl. Crystallogr., 12 (1979) 34.
38 R.D. Shannon, Acta Crystallogr., Sect. A, 32 (1976) 751.
39 W. Schlenk and W. Schlenk, Ber., 62 (1929) 920.
40 A. Wellmar, A. Hallberg and I. Persson, J. Organomet. Chem., 415 (1991) 167.
41 A. Wellmar and I. Persson, J. Organomet. Chem., 415 (1991) 143.