On the Association of the Grignard Reagent

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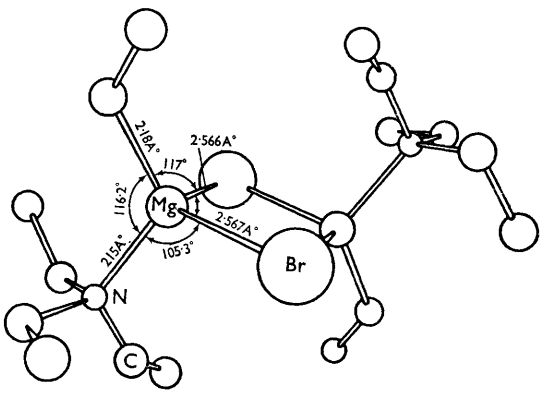
APPARENT molecular weight studies of Grignard reagents have been interpreted in terms of association numbers of one through four[1] depending upon the solvent and the nature of the Grignard reagent. In particular, investigations of organomagnesium solutions[2] indicate that a dimeric species may be present with the general formula $[RMgX{\cdot}S]_2$ and a structure like that of Al_2Br_6. However, the evidence did not distinguish between the many possible isomers with R (alkyl or aryl groups), X (halide), or S (solvent) occupying any of the bridging or terminal positions. In addition, the examples of six-co-ordinate magnesium in $Me_4(OMe)_4MgAl_2(C_4H_8O_2)$[3] and $MgBr_2(C_4H_8O)_4$,[4] five co-ordination in $MeMgBr(C_4H_8O)_3$,[5] and three co-ordination[6] indicate that other geometries cannot be ruled out.

In the solid state, several Grignard reagents with a solvent to RMgX ratio of 1 : 1 have been reported; for example, $MeMgI,(C_5H_{11})_2O$,[7] $C_{10}H_7MgBr,Et_2O$,[8] and $EtMgBr,Et_3N$.[9] Here we report the crystal structure of $[EtMgBr,Et_3N]_2$, which was obtained by preparing ethylmagnesium bromide in n-butyl ether and then adding this solution to triethylamine in the ratio of 2 : 1. Single crystals were grown by slow evaporation of the solvent and gave the following chemical analysis:

	%Mg	%Br	%C	%N	%H
Found:	10·4	32·2	39·6	5·1	8·4
Calc.:	10·80	35·70	42·8	6·24	8·90

A total of 1175 unique reflections were measured with a Picker four circle diffractometer (nickel-filtered Cu-K_α radiation). The structure of the molecule was determined using conventional Fourier and least-squares techniques and has refined to an R factor of 7·6% for the 736 observed hkl and $hk\bar{l}$ reflections. The compound crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions $a = 10{\cdot}468 \pm 0{\cdot}002$, $b = 12{\cdot}673 \pm 0{\cdot}003$, $c = 9{\cdot}414 \pm 0{\cdot}002$ Å, $\beta = 90{\cdot}267° \pm 0{\cdot}04$, $U = 1248{\cdot}84$Å^3, $D_m = 1{\cdot}22$, $D_c = 1{\cdot}20$ for 2 molecules of $[EtMgBr,Et_3N]_2$ per unit cell.

The molecule, shown in the Figure, lies on a



FIGURE

crystallographic inversion centre. The bridging magnesium bromine distances of 2·56 and 2·56 Å are about 0·1 Å longer than the single bond magnesium–bromine distance found in $MgBr_2$,-4THF,[4] $PhMgBr,2C_4H_{10}O$,[10] $EtMgBr,2C_4H_{10}O$,[11] and $PhMgBr,2C_4H_8O$.[4] This lengthening of the metal–bromine distance compares favourably with the bridging magnesium bromine distances of $2{\cdot}60 \pm 0{\cdot}02$ Å in $Mg_4Br_6O,4(C_4H_{10}O)$.[12]

The formation of the dimeric rather than the monomeric species can be attributed to steric factors in that the environment of a magnesium atom co-ordinated to two bromine atoms, one triethylamine molecule, and one ethyl group is considerably less crowded than the environment about a di-solvated monomeric species. In fact,

the *trans*-form observed is favoured over all other possible dimeric species with four-co-ordinate magnesium for this reason. The degree to which association occurs in solution at a given concentration undoubtedly depends to a great extent on the size of the organic group and the solvent used. The existence of $MeMgI(C_5H_{11})_2O$[6] and $C_{10}H_7MgBr\text{-}Et_2O$[7] tend to substantiate this point of view. It should be re-emphasized, however, that unless precautions similar to those described by Vreugdenhil and Blomberg[1] are taken, the Grignard reagents are easily oxidized and associated species, such as $Mg_4Br_6O,4(C_4H_{10}O)$,[12] may also be present.

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