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THREE-COORDINATE MAGNESIUM

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CONTENTS

A. INTRODUCTION

(i) General

Definitions of the term, coordination number, have evolved from the well-known coordination theory first proposed by Werner in 1891. Coordination number can be defined * as the number of species coordinated to a central atom or ion. The species can be atoms, molecules or ions. According to Bailar [1] and O'Brien [2] the definition of coordination number for the crystalline state differs. In crystals, it refers to the number of atoms or ions which surround the central atom or ion in question which are at equal distances from it, no matter what the nature of the bond between them [1] or according to O'Brien's definition [2], to the number of nearest neighbors of an atom in the crystal and is dependent only on the radius ratio.

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* Adapted from definitions in refs. 1—4.

Currently there is a great deal of interest in elucidating the factors relating to the various states of coordination possible for elements in their different compounds, particularly at the extreme limits of coordination-high coordination states and low coordination states and in compounds with odd coordination numbers, since these are relatively uncommon [5]. In fact, it has been recently stated [6] that, "One of the major goals of inorganic chemistry is to prepare compounds of elements in unusual oxidation states." The factors as they pertain to different elements have not as yet been completely determined and satisfactory explanations have not yet been generally accepted. Although there are numerous examples of the three-coordinate state for non-metallic elements, those for metallic elements are rare [2,4,5,7]. For these reasons, the three-coordinate state of magnesium is of considerable interest.

Although the most common state of coordination for magnesium is four [8—11], examples of five- [12,13], six- [14—17], and eight-coordination [18,19] have also been reported. Although ionic species undoubtedly occur in the equilibria postulated for various solutions, even though some of these can be formally considered as "three-coordinate", they are not discussed here since they would be solvated in the highly basic and polar solvents in which they are detected, and since these are generally thought to be minor constituents of the equilibria.

With regard to three-coordinate magnesium, although possible examples appear in the literature since about 75 years ago, some structures were suggested without adequate supporting evidence and were later shown to be incorrect. Only in relatively recent times, however, has definitive work appeared with evidence in support of some compounds containing three-coordinate magnesium. The present paper is a review of the published papers with emphasis on the experimental evidence presented in more recent work. The older literature is only briefly reviewed for an overall perspective. The review is intended to be an overview of the present status of three-coordinate magnesium and hopefully will help to stimulate further research into this area. Some of the papers on four-coordinate magnesium are briefly discussed when they are directly involved in the evolution of structures for the three-coordinate state. Although a review on three-coordinate magnesium compounds has never appeared, a large number of reviews on the general topic of the structure and constitution of organomagnesium compounds have been published [20—51], in particular, focusing on the Grignard reagent in which there has been renewed interest possibly centered around the centennial anniversary celebrations in 1971 of the birth of V. Grignard. References have been checked through Vol. 85 (1976) Chemical Abstracts indices.

(ii) Priority considerations

Since there seems to be some confusion [52—54] over the question of the first claim to the discovery of three-coordinate magnesium in a compound, a few words on this subject might be appropriate here as it relates to the present topic. Priority is sometimes difficult to decide and the subject more complicated than it might appear from initial assessments. Traditionally, date of receipt by a journal has been the deciding factor where two or more groups have equal claim to priority. However, the situation is frequently more complex. Thus, how should oral presentation be ranked in priority? Should appearance in a thesis or dissertation (but otherwise unpublished) be accepted as equivalent to journal publication? Should it be at the postulation stage if later evidence substantiates the postulated structure? Or should priority go to the first one to prepare the compound even though inconclusive proof of structure or even an incorrect structure is given? Or should priority go to workers who present conclusive analytical and structural proof. Also, the question as to what would be acceptable as conclusive evidence enters in. What might be acceptable evidence at one time might not be at some later date as better methods, techniques and instrumentation become available. Analysis of the basis of the Nobel prize awards would be instructive with respect to the points discussed above. It is not proposed here to make a decision as to what the criteria should be. It may be more illuminating to present the development of the topic in an historical perspective so that the reader can make a more informed judgement based on assessment of validity of the evidence presented. Three-coordinate magnesium presents an interesting case in point.

B. ORGANOMAGNESIUM HALIDE ETHERATES *

Barbier [55] was the first to prepare an alcohol by mixing together methyl iodide, a ketone, magnesium and ether using the general method of Saytzeff but substituting magnesium for zinc. However, Grignard [56,57] was the first to separate the reaction into two steps, the first being the reaction of alkyl halide and magnesium in ether ** to form the reagent that now bears his name and the second being the reaction of the reagent with a ketone or aldehyde to form the corresponding alcohol after hydrolysis. Grignard [60] and Blaise [61] noted that when the solutions of organomagnesium halides prepared in ether were evaporated and dried, one molecule of ether per molecule of organomagnesium halide was retained with great tenacity. Grignard [60] and Blaise [61] formulated the reagent as a monoetherate $RMgX \cdot (C_2H_5)_2O$, Grignard suggesting that ether played a role analogous to that of water of crystallization in hydrates. Related to these organic compounds, a corresponding crystalline inorganic monoetherate having the

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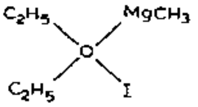
* A more complete review of the older work is in Kharasch and Reinmuth [20] which thoroughly references the older work up to that time.

** Hallwacks and Schafarik [58] apparently were the first to prepare an organomagnesium compound by heating ethyl iodide with magnesium in the absence of ether; however, structures were not suggested in their paper, structural theories having only been suggested independently by Couper and Kekule the preceding year. For a brief historical review of the magnesium/organic halide reaction see ref. 59.

composition, $MgBr_2$, $(C_2H_5)_2O$ was later prepared by Zelinsky [62] by reacting together bromine, magnesium and ether and allowing the liquid product to stand over sulfuric acid.

Baeyer and Villiger [63] proposed structure 1 for the non-crystalline solid they obtained on the removal of diethyl ether in vacuo at 80° from a solution of methylmagnesium iodide. At that time quadrivalent structures for oxonium compounds were in vogue. Zerewitinoff [64] later noted that all of the etherates prepared up to that time were non-crystalline and reported that when diamyl ether was used as solvent, a crystalline diamyl monoetherate of methylmagnesium iodide was obtained for which a structure analogous to 1 was written. Grignard [65,66] accepted this type of structure but preferred formulations such as 2 as being more consistent with the mode of reaction of the compounds. Chelintzev * at first accepted structure 1 and even proposed a two-step mechanism for its formation. He also reported that organomagnesium compounds could be prepared in benzene [67] containing a small amount of ether, anisole or tertiary amine, or in light petroleum ether [68] with a few drops of dimethylaniline or even in benzene or toluene alone at a high enough temperature [67]. He also used structure 1 at first in connection with his thermochemical studies in which he reported [68] the same amount of heat evolution for the reaction of solid organomagnesium compounds with ether as for compounds prepared in benzene or light petroleum in the presence of a small amount of dimethylaniline and this solution then added to ether in a calorimeter. In addition to structure 1 he later considered [68] structure 2 and suggested an additional structure 3 based on Werner-type complexes [1,69].



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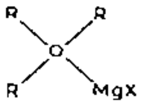

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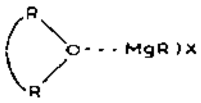

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Since magnesium iodide was reported [62] to form a dietherate, $MgI_2 \cdot 2(C_2H_5)_2O$, he considered the analogous possibility for the Grignard reagents and later reported [70] thermochemical evidence for dietherates as an addi-

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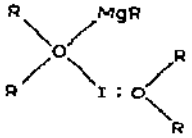
* The transliterated name has been spelled in several different ways in different journals and even in the same journal: W. Tschelinzeff, Chem. Ber., C.R. Acad. Sci., Paris, J. Chem. Soc. Abstr. and Chem. Abstr., 1907; W.V. Tschelinzeff, Chem. Abstr., 1907—8; V. Tschelintsev, Chem. Abstr., 1908; V. Tzchelinzeff, Chem. Abstr., 1908; V. Chelintzev, Chem. Abstr., 1908—1915; V.V. Tschelincev, J. Chem. Soc. Abstr., 1913; W. Tchelinzef, C.R. Acad. Sci., Paris, 1907. Although W. Tschelinzeff is the spelling used by most of the journals, the one used consistently later by Chem. Abstr. is the one used in this paper.

tional type of organomagnesium compound. Propylmagnesium iodide and isoamylmagnesium iodide were prepared in diethyl ether and the excess ether removed by distillation. The weights of the products corresponded to dietherates, $RMgI \cdot 2(C_2H_5)_2O$. In addition, when ether was added to solutions of the above alkylmagnesium iodides in benzene, substantial heat was evolved for the first two moles of ether added but there was little heat evolution for subsequent ether additions. Determinations of heat evolved from hydrolysis of Grignard reagents furnished additional evidence [71] for the dietherate formulation. Structure 4 was proposed for the dietherates.



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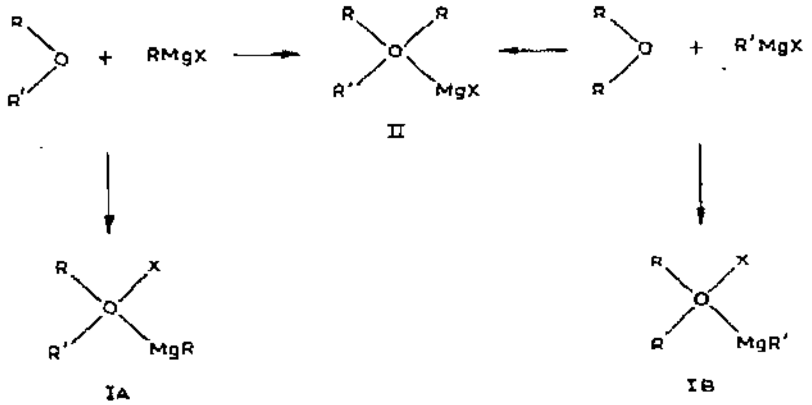
In attempting to differentiate between the two structures 2 and 3 postulated for the monoetherates, Chelintzev prepared a series of Grignard etherates using mixed ethers and determined the heat evolved on hydrolysis. He reasoned that on the basis of Grignard's structure 2 on combining with ether, the same compound would be obtained, whereas different compounds (1A and 1B) would be obtained on the basis of the Baeyer structure as shown (Scheme 1). However, in determining [72] the heat of hydrolysis of a number of organomagnesium iodides complexed with ethers, the differences in thermal effects were considered too small to be able to formulate any definite conclusion regarding structures. He thought that he was able to decide [73] between the two in favor of the Baeyer structure on the basis of hydrolysis studies in which he obtained gaseous ethane from the compound prepared from ethylmagnesium iodide in ethyl amyl ether but liquid pentane from amylmagnesium iodide in diethyl ether (eqns. (1) and (2) respectively). Experiments with two other pairs of compounds substantiated



Scheme 1

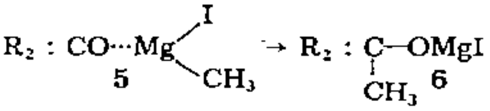
$$C_2H_5(C_5H_{11})O : (I)MgC_2H_5 + H_2O \rightarrow C_2H_6 \tag{1}$$

$$(C_2H_5)_2O : (I)MgC_5H_{11} + H_2O \rightarrow C_5H_{12} \tag{2}$$

this conclusion. Stadnikov [74—78] thought he had evidence in favor of the oxonium intermediate 2 when he isolated products from the recombination of various readily cleavable ethers with the alkyl from the alkyl halide (eqn. 3). However, Gorskii [79,80] stated that the same conclusions could

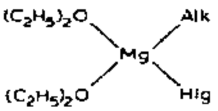
$$\text{n-}C_4H_9OCHPh_2 + \text{n-}C_3H_7I \xrightarrow[(2)\,H_2O]{(1)\,Mg} \underset{(12.5\%)}{C_3H_8} + \underset{(14.5\%)}{Ph_2CHCHPh_2} + \underset{(35.0\%)}{Ph_2CHC_3H_7} \tag{3}$$

be drawn on the basis of either formula and since reductions of ketones to alcohols by alkyl iodide—magnesium can occur in dry toluene in the absence of ether, reduction of ethers by alkylmagnesium iodide to alkane + alkane + alkoxymagnesium iodide obviates the necessity of assuming etherates as intermediates. Chelintzev [81] characterized these reactions as involving ether cleavage which resulted only by the action of water [81]. Moreover, Thorp and Kamm [82] isolated a 61% yield of benzene from the reaction of bromobenzene and magnesium in ether and subsequent hydrolysis and less than 0.2% of ethane; benzoic acid was the sole product isolated from the carbonation of this reaction mixture. On the other hand, they reported a 97% yield of ethane from the reaction of ethyl bromide and magnesium in ethyl phenyl ether followed by hydrolysis; no benzene was found. From the carbonation of the reaction mixture they isolated propanoic acid and no benzoic acid. By analogy with a proposed mechanism of the reaction of ketones with phosphorus pentachloride, for the addition reactions of organomagnesium halides with ketones, Strauss [83] in a footnote suggested a prior coordination of the magnesium of the organomagnesium halide to the oxygen as shown in structure 5 followed by a shift of the alkyl group to carbon to form the addition product 6 (eqn. 4). This was modeled after the mode of



$$\underset{5}{R_2 : CO\cdots Mg\overset{I}{\underset{CH_3}{<}}} \rightarrow \underset{6}{R_2 : \underset{CH_3}{C}\!-\!OMgI} \tag{4}$$

reaction of phosphorus pentachloride with unsaturated ketones [83]. Combining the idea of a Werner-type coordination complex suggested by Chelintzev [68] with that of Strauss [83], Meisenheimer and Casper [84]



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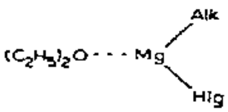

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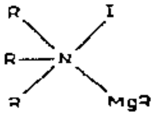
proposed structure 7 for the dietherates of alkylmagnesium halides and also proposed mechanisms and structures for their addition reactions and products formed. Although they did not consider monoetherates, presumably they would have structure 8 analogous to 7.

C. ORGANOMAGNESIUM HALIDE AMINATES *

Chelintzev [85] pointed out the analogy between organic oxygen and nitrogen compounds in connection with his use of tertiary amines for the preparation of Grignard reagents. He used thermal studies [86] to show that only monosolvated Grignard reagents $RMgI \cdot NR_3$, were formed with tertiary amines and no disolvated species as with ethers. Analogous to the monoetherates two possible structures were proposed for the monoaminates, 9 and 10.



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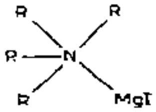

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Since organomagnesium halides can form dietherates whereas only monoaminates are formed, by determining the heat evolved from reactions of Grignard aminates with ethers and mixed Grignard etherate—aminates with ethers, Chelintzev [87] obtained evidence for the presence of intermediate compounds such as $RMgI \cdot NR_3 \cdot R_2O$.

In 1965, Ashby [88] prepared ethylmagnesium bromide in triethylamine and fractionally crystallized the product from triethylamine. Although ethylmagnesium bromide crystallized as the bis-solvate **, on drying under high vacuum the monosolvate, $C_2H_5MgBr \cdot N(C_2H_5)_3$, was obtained. In accord with this formulation a 1 : 1 : 1 Mg : Br : N ratio was obtained for all fractions. Molecular association measurements in triethylamine at 35°C (determined ebullioscopically at 150 torr) showed that only a monomer was present over a wide concentration range. When ethyl bromide and magnesium were reacted in diethyl ether and this solution added to triethylamine, the same product as above was isolated in over 90% yield. It should be noted that since the molecular association measurements were made in triethylamine, the disolvated species, $C_2H_5MgBr \cdot 2\ N(C_2H_5)_3$, (if formed) having

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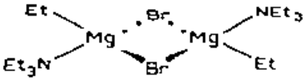
* The term aminate is adopted here for the class of coordination compounds which coordinate with amines. This is analogous to the use of the term hydrate for complexes with water and etherates for complexes with ethers. In comparison, it should be noted that Werner [69] first used the term ammonate to refer to complexes with ammonia; this term was later replaced by the term ammine by Werner [1,69].

** It is not clear from the paper whether this substance was actually characterized as the bis-solvate. Chelintzev in his thermochemical studies [86] came to the conclusion that only the monosolvate was formed.

four-coordinate magnesium, would be present. It has been stated [30] that the mono-amine complex is a dimer in benzene solution, presumably containing a $MgBr_2Mg$ bridge according to a personal communication from Ashby [89].

In a study of the solid-state structure of the monosolvate, Toney and Stucky [90] obtained it by preparing ethylmagnesium bromide in n-butyl ether and adding this solution to triethylamine in a 2 : 1 ratio. Single crystals grown by slow evaporation of solvent gave the correct analysis for EtMgBr, Et_3N. By a single crystal X-ray diffraction study they determined the structure to be a *trans* dimer (11) with bridging through the bromine atoms. The formation of a dimer rather than the monomeric species was attributed to steric factors in that the environment of a magnesium atom coordinated to two bromine atoms, one triethylamine molecule and one ethyl group is considerably less crowded than the environment about a disolvated monomeric species. The *trans* form which was found, is favored over all other possible dimeric species with four-coordinate magnesium for this reason according to the authors.



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Ashby and Reed [91] prepared the following organomagnesium halides each complexed with one equimolar amount of triethylamine in benzene (% yields in parentheses): EtMgCl(97), EtMgBr(88), EtMgI(97), n-BuMgCl-(93), PhMgBr(77). The Mg : X : N ratio for all of these was determined to be 1 : 1 : 1 within experimental error. Ashby and Walker [92] later prepared a number of alkylmagnesium chlorides, bromides and iodides directly in triethylamine solution and also determined for these a 1 : 1 : 1 Mg : X : N ratio.

Although it appears that the organomagnesium halide aminates prepared up to the present time are dimers in the solid state or in solution, it is possible that with a greater degree of steric bulk in the organic group and/or the amino group, monomers which would have three-coordinate magnesium might be obtained analogous to results with other classes of compounds described below.

D. ALKYLMAGNESIUM AMIDES *

Coates and Ridley [53] investigated products from reactions of dialkylmagnesium and secondary amines in which an alkane is eliminated

$$R_2Mg + R'_2NH \rightarrow RH + (RMgNR'_2)_x$$

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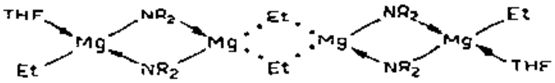
* This term is used to describe metallic substitution products of amines following the usage by Wakefield [32].

Where R and R′ groups were small, for example R = Et and R′ = Me, insoluble products (apparently polymeric) were obtained. With R = iPr or Et and R′ = Et, products were obtained which contained complexed diethyl ether (used as solvent) which could not be removed but was displaced by tetrahydrofuran. Complexed tetrahydrofuran was clearly evident in the infrared spectra of the viscous liquid products designated as $(\mathrm{EtMgNR_2})_2 \cdot \mathrm{THF}$. The apparent molecular weights of these products by cryoscopy in benzene indicated some association in solution. The monomers would contain one three-coordinate and one four-coordinate magnesium atom unless both lone pairs of tetrahydrofuran are used for coordination according to the authors. The dimers were formulated as 12 on the basis of four-coordinate magnesium.



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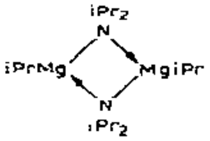
From the reaction of diisopropylmagnesium and diisopropylamine, an ether-free product was obtained which was extremely soluble in hexane and dimeric in benzene and was therefore formulated with three-coordinate magnesium. Proton NMR spectra in benzene showed doublets at τ 8.885 and 8.99($\mathrm{NCH\underline{Me}_2}$) and 8.49 and 8.62($\mathrm{MgCH\underline{Me}_2}$) and septets at τ 6.78—7.44-($\mathrm{N C\underline{H}Me_2}$) and 9.51—10.32($\mathrm{MgC\underline{H}Me_2}$). Of two possible structures, the authors preferred 13 because nitrogen bound to an electropositive element such as magnesium is likely to act as a strong electron donor and thus to be a much better bridging atom than carbon. However, structure 14 or a structure containing one N and one carbon bridge were not altogether eliminated.



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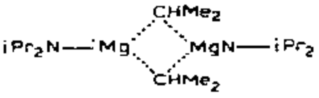
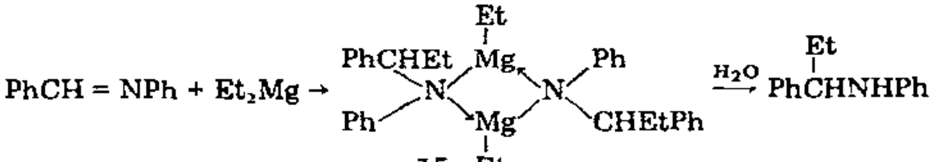


14

A crystalline dimer was obtained by displacement of one ethyl group from diethylmagnesium by reaction with 2,2,6,6-tetramethylpiperidine but again Coates and Ridley could not distinguish between structures analogous to 13 and 14. Although molecular models suggested at least two magnetically



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$$\mathrm{PhCH{=}NPh + Et_2Mg} \rightarrow \mathbf{15} \xrightarrow{\mathrm{H_2O}} \mathrm{Ph\overset{Et}{C}HNHPh} \qquad (5)$$

distinct sets of methyl groups in the complex, only one methyl resonance (τ 8.59) was observed in benzene solution.

From the reaction of benzylideneaniline and diethylmagnesium (eqn. 5), a crystalline ether-free product, dimeric in benzene was isolated. The expected secondary amine was obtained by hydrolysis. Structure 15 is tentatively postulated for the product.

The authors stated that although the three amino(alkyl) dimers described in their paper must contain three-coordinate magnesium, it is possible that they associate in the crystalline state despite steric hindrance.

E. DIALKYLMAGNESIUM

Solvent-free dimethylmagnesium was reported to have been prepared in 1929 [93,94]. A crystal structure study in 1964 [95] however, showed that the compound forms high polymer chains with methyl bridges between the magnesiums. An X-ray powder diffraction study of diethylmagnesium also showed [96] a polymeric chain structure with bridging methylene groups and tetrahedral coordination of the magnesiums. The compound was prepared via the Schlenk equilibrium [97] from an ether solution of ethylmagnesium chloride by precipitating magnesium chloride with dioxan, evaporating the solvent, recrystallizing the residue from ether, and drying the etherate in vacuo at 100°C to obtain a microcrystalline powder. Several other solvent-free dialkylmagnesiums have been prepared [98]. Since they are also relatively insoluble and non-volatile, polymeric structures are inferred.

Glaze and Selman [99] reported the preparation of di-n-pentylmagnesium by the reaction of magnesium metal and dialkylmercury in benzene. The benzene solutions were largely dimeric as measured cryoscopically. However, Glaze and Selman did not suggest any structures for the dimers. It is evident that structures containing three-coordinate magnesium like those proposed by Kamienski and Eastham [100] (see below) are possible. Diethylmagnesium monoetherate $(C_2H_5)_2Mg \cdot (C_2H_5)_2O$ was reported [101,102] to have been prepared by reacting diethylmercury and magnesium in ether. An elemental analysis checked for the monoetherate; however, no molecular weight determinations were carried out. On the basis of the crystal structure studies of Weiss [95,96] on dimethyl- and diethylmagnesium where magnesiums were bridged by alkyl groups, and the X-ray single crystal structure determination of the monoaminate of ethylmagnesium bromide, C_2H_5MgBr, $(C_2H_5)_3N$, by Toney and Stucky [90] where bridging of magnesiums via bromines was found to form dimers, in the diethylmagnesium monoetherate, bridging through oxygen (16) methylenes (17) * or a combination of oxygen and methylene (18) might be expected for solids analogous to suggestions of

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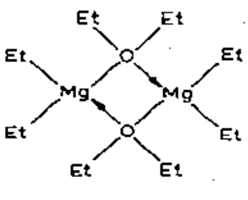
* *Cis/trans* isomers are possible; *trans* is shown.



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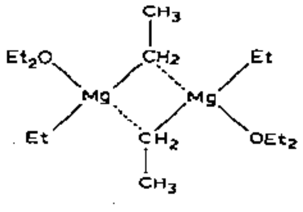

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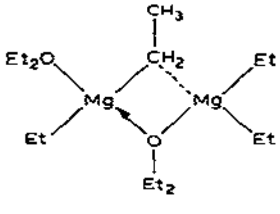

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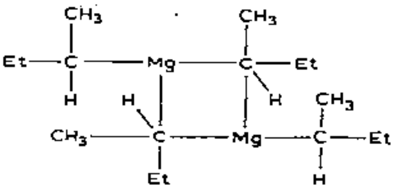
Coates and Ridley [53]. In addition higher polymers can be visualized as possible.

Although diphenylmagnesium has also been reported to have been prepared, [103—105] it is insoluble in benzene. No structural determinations appear to have been carried out.

Kamienski and Eastham [100] described the preparation of unsolvated di-sec-butylmagnesium by direct reaction of magnesium metal and sec-butyl chloride in hydrocarbon solvents such as hexane to which a limited amount of an ether (such as dimethyl ether) was added. The product was desolvated (freed of ether) by codistillation with benzene or cyclohexane. The nonsolvated compound was a mobile liquid completely miscible with hydrocarbons, this property distinguishing it from all previously characterized magnesium alkyls. The compound was characterized by vapor-phase chromatography of sec-butyl alcohol obtained from air oxidation of organic solutions before and after hydrolysis, titration of solutions and NMR of solutions. The degree of association in cyclopentane as measured by osmometry was approximately two for concentrations of 0.09—0.36 M. The structure suggested by the authors is 19. Work in progress at the time by the authors established that di-t-butylmagnesium was also miscible with hydrocarbons and was expected to be dimeric. The restricted ability of the dialkylmagnesium compounds to self-associate was attributed by the authors to steric hindrance imposed by the presence of both an α- and a β-methyl group.



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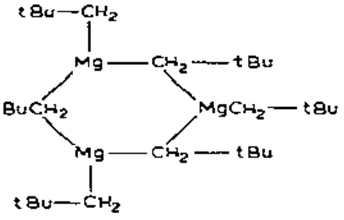
More recently Anderson and Wilkinson [106] prepared bis(neopentyl)-magnesium by a slight modification [107] of the Schlenk disproportionation of a Grignard reagent with dioxan [97]. The dialkylmagnesium is soluble in diethyl ether and the dioxan complex of magnesium chloride is insoluble. Removal of dioxan under reduced pressure yielded the base-free dialkylmagnesium contaminated with trace quantities of chloride. The neopentyl compound was freely soluble in benzene and sublimed at 110°C in vacuo in contrast to bis(trimethylsilylmethyl)magnesium, $Mg(Me_3SiCH_2)_2$ and bis(2-methyl-2-phenylpropyl)magnesium, $Mg(PhMe_2CCH_2)_2$, which were insoluble in hydrocarbon solvents, non-volatile and thermally stable to at least 200°C. The neopentyl compound was found to be trimeric by cryoscopy in benzene under nitrogen. Two reasonable alternatives were proposed for the structure of the trimer. In structure **20** each magnesium is 3-coordinate, being bonded to a terminal alkyl group and to two bridging alkyl groups by way of a 3-center two-electron bond. In the other alternative, **21**, the central magnesium atom is 4-coordinate and the other two are 3-coordinate.



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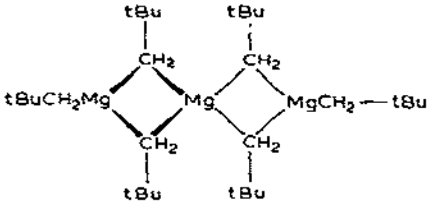


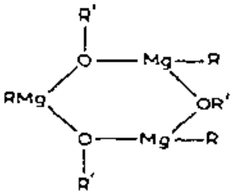
21

The ^1H NMR spectrum consisted of only two resonances due to the t-butyl and methylene protons at room temperature. Lowering the temperature to —90°C resulted only in line-broadening and was not diagnostic. The ^{13}C-[^1H] NMR spectrum in [$^2H_8$]toluene at room temperature consisted of three resonances at δ 36.57, 33.03 and 30.75 (δ defined as p.p.m. to the high-frequency side of $SiMe_4$). The proton-coupled spectrum consisted of a quartet (δ 36.57), a triplet (δ 33.03) and a singlet (δ 30.75) which are assigned to the methyl, methylene and quaternary carbons, respectively. Cooling the sample to —80°C caused the resonances to broaden, an indication that bridge-terminal exchange is rapid at this temperature on both ^1H and ^{13}C NMR time scales.

The marked difference between bis(neopentyl)magnesium and its silicon analog, $Mg(Me_3SiCH_2)_2$, was ascribed to steric hindrance, silicon being larger than carbon, thus minimizing the steric congestion about the metal atom and allowing the latter to be 4-coordinate while keeping the coordination number of the former less than four. This was supported by the observation that $Be(Me_3SiCH_2)_2$ is dimeric though $Be(Me_3CCH_2)_2$ exists in a monomer—dimer equilibrium in benzene solution [108].

F. ALKYLMAGNESIUM ALKOXIDES

Ethylmagnesium ethoxide was reported by Vreugdenhil and Blomberg [109] to be trimeric in diethyl ether as determined by quasiisothermal distillation. A six-membered ring structure **22** (R = Et; R′ = Et or Br) was proposed. Since the measurements were made in diethyl ether, additional coordination of the magnesiums by ether is probable.



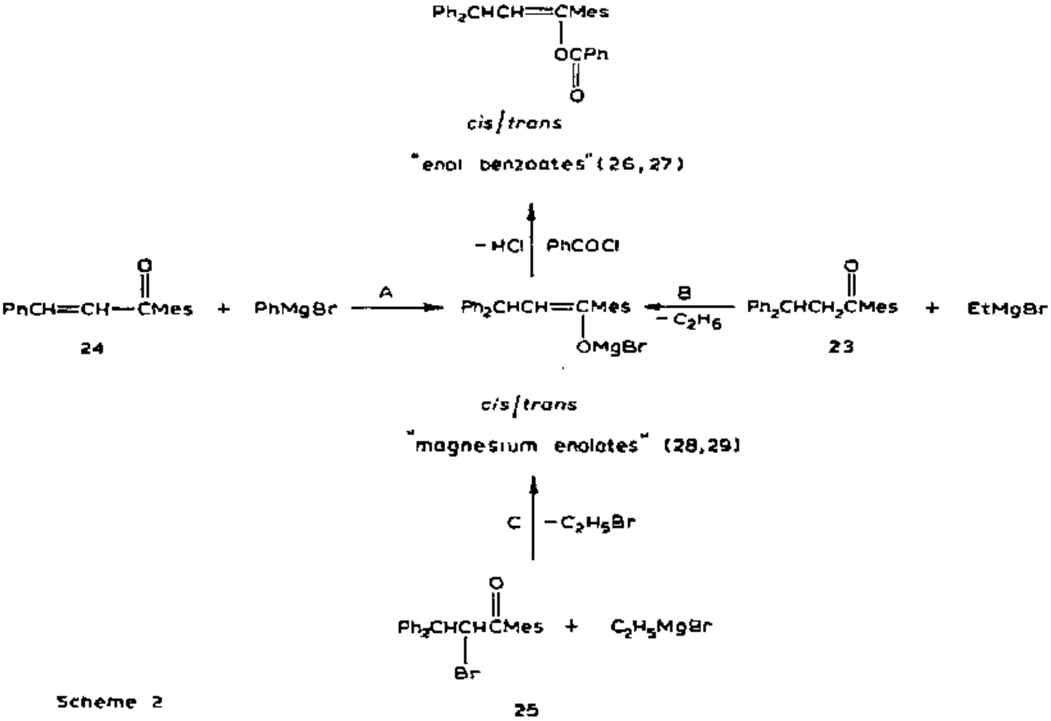
22

Bryce-Smith and Graham [110], however, reported that by cryoscopy in benzene n-butylmagnesium isopropoxide was trimeric; the values were invariant over a period of three days. The structure proposed (22; R = n-Bu, R′ = i-Pr) contains three-coordinate magnesium. Bryce-Smith and Graham suggested Mg-π-bonding which was considered to arise from overlap of the *p*π-component of the occupied *n*-orbital on oxygen with a vacant orbital on adjacent magnesium. Such π-bonding would be expected to lead to a flattened version of a "chain" or "boat" structure. Evidence for π-bonding in the system resides in the observation that when diethyl ether was added to a benzene solution of n-butylmagnesium isopropoxide followed by removal of solvents below 20°C under reduced pressure, a product was obtained from which less than 10 mol% of ether was produced on hydrolysis. Thus, the tendency for solvation with diethyl ether was very slight, the magnesium exhibiting very weak electron acceptor properties. The procedure used to prepare the organomagnesium alkoxides was to add a mixture of a primary alkyl or aryl chloride (2 mol) and the appropriate alcohol (1 mol) to fresh magnesium powder (2.5 g atom) with stirring in refluxing methylcyclohexane under nitrogen. The reaction was initiated with an iodine crystal. Heating under reflux was continued until the solution was chloride-free. The following organomagnesium alkoxides were prepared by this procedure (% yields in parentheses): n-BuMgOEt(98), n-BuMgO-nPr(98), n-BuMgO-iPr(80), n-BuMgO-sBu(90), n-C_6H_{13}MgO-iPr(50), PhMgOEt(50).

At about the same time Coates and Ridley [53] reported that ethylmagnesium isopropoxide, ethylmagnesium t-butoxide and isopropylmagnesium isopropoxide were tetrameric by cryoscopy in benzene whereas ethylmagnesium n-propoxide, isopropylmagnesium methoxide and isopropylmagnesium ethoxide were oligomers having degrees of association of 7—8.4 in benzene. By analogy with the corresponding zinc compounds, they suggested [53] that the tetramers may have cubane-type structures (containing four-coordinate magnesium). They prepared the alkoxides from the dialkylmagnesium diethyl etherate and the appropriate alcohol with subsequent removal of all the ether. The authors noted that the tetramers were obtained only when there was chain-branching at the carbon α to oxygen. With the less-hindered cases, higher oligomers were formed. The authors suggest the possibility that with a sufficient degree of steric hindrance, dimeric alkoxides might be formed as they found [53] with secondary aminomagnesium alkyls. As pointed out by Bryce-Smith and Graham [110], apparently the degree of association is very sensitive to the nature of the organic groups and/or the method of preparation [32,53].

G. MAGNESIUM ENOLATES

The preparation of the first compounds for which evidence of three-coordinate magnesium was later presented * was reported by Kohler et al. [112]. They prepared the bromomagnesium derivative of 2,2-diphenylethyl 2,4,6-trimethylphenyl ketone 23 by three routes (Scheme 2): (A) 1,4-addition of phenylmagnesium bromide to benzalacetomesitylene 24; (B) action of Grignard reagent on 23; (C) action of Grignard reagent on 2,2-diphenyl-1-bromoethyl 2,4,6-trimethylphenyl ketone 25. They noted that the magnesium compounds prepared by route A vs. those from routes B and C formed stereoisomeric (*cis/trans*) enol benzoates 26 and 27 in high yields on reaction with benzoyl chloride. A high melting benzoate (162°C) was formed by the first method and a lower melting benzoate (142°C) by the other two methods (Scheme 2). They formulated the magnesium compounds as isomeric magnesium enolates and carried out elemental analyses on the enol



Scheme 2

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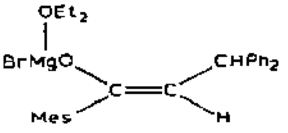
* Previously the first such compound prepared for which evidence of three-coordination was later presented [54] was the magnesium enolate prepared by Fuson et al. [111].

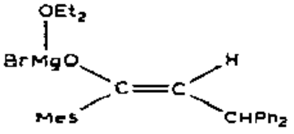
benzoates but not on the corresponding magnesium enolates.

Nesmeyanov et al. [113] performed elemental analyses in the bromomagnesium compounds from routes A and B which showed that they each contained one mole of ether. These compounds were shown to differ in their solubilities in benzene, that from route A being about ten times as soluble as the one from route B. They also differed in chemical reactivity, only the one from route A oxidizing to peroxide by molecular oxygen. However, both isomers formed the same ketone on hydrolysis.

Nesmeyanov et al. [113] stated that they were able to destroy the isomerism of the magnesium enolates by adding tetramethylammonium iodide, heating for four hours and then adding benzoyl chloride with heating. The same benzoate (m.p. 143°C, 31% yield from enolate A; m.p. 144—145°C, 37% yield from enolate B) was obtained from both magnesium enolates. On the basis of their studies, Nesmeyanov et al. concluded that mesomeric anionic forms were excluded for the magnesium enolates. However, neither the Kohler nor Nesmeyanov groups were able to assign *cis/trans* structures to the isomeric magnesium enolates of enol benzoates and the molecular states of aggregation of the former were not determined. More recently, cryoscopic determinations in naphthalene carried out [114] on the isomeric magnesium enolates showed that they were both monomeric at concentrations of 8—12 wt% for the more soluble and 2% for the less soluble isomer with no discernible trend toward association at these concentrations. Cryoscopy results in benzene also showed monomeric species. Infrared spectra (in mineral oil) confirmed the enolic nature of the magnesium enolates. From ^{1}H NMR spectra on the corresponding enol benzoates, the *cis—trans* structures for the magnesium enolates were assigned as *Z*(28) from route A and *E*(29) from routes B and C.

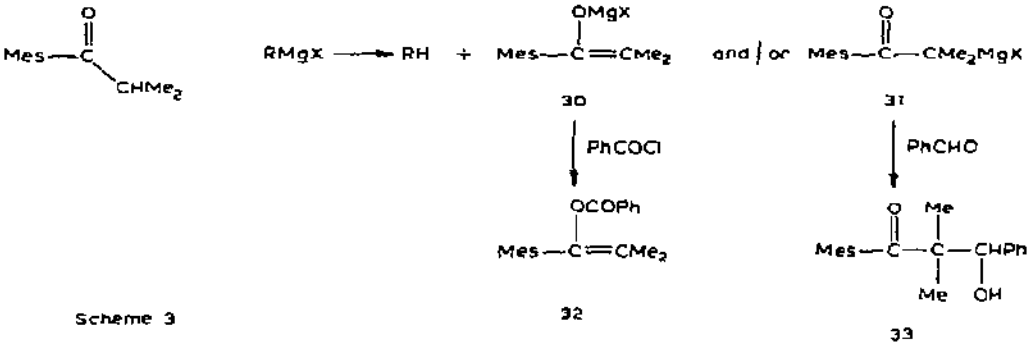


Z (via route A)
28



E (via routes B & C)
29

On reacting isopropyl mesityl ketone with Grignard reagents, Fuson et al. [111] prepared the intermediate which could have an enolate structure (30) reacting through condensation reactions by *O*-substitution (indicative of an enolate (30)) or *C*-substitution (from a keto structure (31)) (Scheme 3). Thus, for example, with benzoyl chloride, only the *O*-acylation product, the enol benzoate (32) was isolated whereas with benzaldehyde, the carbonyl addition product (33) was obtained, presumably via the keto Grignard structure (31). The two modes of reaction were thought to take place via an equilibrium between the enolate (30) and keto (31) forms. Fuson et al. [111] assumed the enolate as the major structure for the magnesium-con-



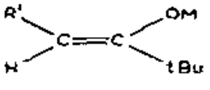
Scheme 3

taining intermediate; however, they did not analyze or attempt to characterize this intermediate.

The organomagnesium intermediate was more recently [54] isolated and characterized as the magnesium enolate (30) as follows. The compound was prepared by reacting isopropyl mesityl ketone with an ether solution of ethylmagnesium bromide; the precipitated derivative was recrystallized from benzene. Elemental analysis and analysis for isopropyl mesityl ketone from hydrolysis checked accurately for a structure containing one diethyl ether group per organomagnesium grouping. Molecular weight determinations by cryoscopy in naphthalene and benzene checked for a monomer; the values showed no definite trend with concentration. The infrared spectrum of a mineral oil mull showed absence of a carbonyl stretching band excluding the keto structure (31) and presence of a C=C (enolic) stretching band. The ^{1}H NMR spectrum in benzene (for X = I) showed the coordinated ether as a triplet—quartet combination centered at 0.96(CH_3) and 3.43(CH_2) (J = 6.7—6.8 Hz) and singlets for o-CH_3 at 2.51; p-CH_3 at 2.14; CH_3(*cis* to enolic O) at 2.04; CH_3(*trans* to O) at 1.38 (δ values in p.p.m. from TMS).

Since the corresponding organomagnesium compound from methyl mesityl ketone was found [115] to be predominantly dimeric at comparable concentrations, the additional methyl groups in the organomagnesium compound from isopropyl mesityl ketone evidently provide steric bulk which inhibits dimer formation. It should be emphasized that structural considerations here apply to solutions in the solvents in which ^{1}H NMR spectral and cryoscopic measurements were made (benzene and naphthalene). It should be noted, however, that since infrared spectra were on the solid state as a mineral oil mull, both monomer and dimer would have enolate groupings.

Fellmann and Dubois [116] more recently used ^{13}C NMR to investigate the structures of metallic enolates of type 34. The spectrum of the sym-



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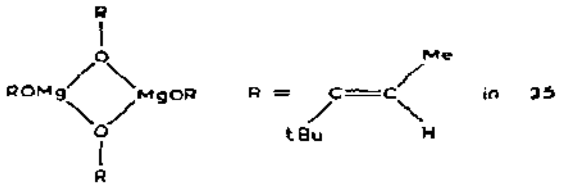

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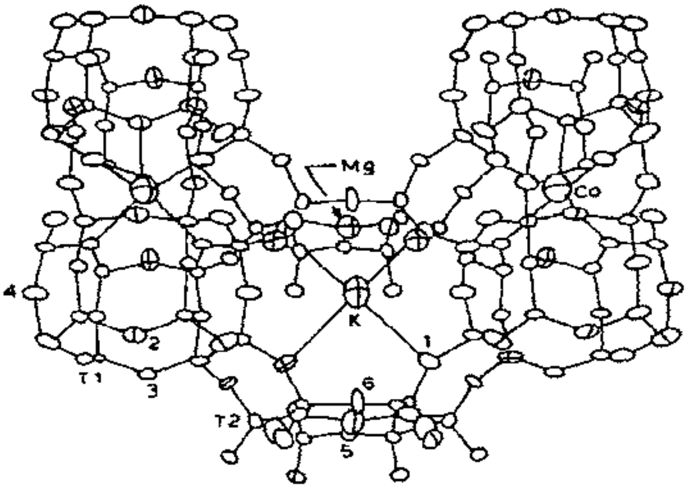
metrical magnesium derivative $(RO)_2Mg$ of t-butyl ethyl ketone revealed a mixture of two *O*-metallated entities. The difference between these was not attributed to solvation of magnesium by 1,4-dioxan since the *sp*^{2} carbon signals were unchanged with a large excess or absence of dioxane in the solution. On the basis of an equipartition of the enolate part on two non-equivalent sites, structure 35 was postulated for the symmetrical enolate. The authors emphasize that the spectrum unambiguously indicates the absence of any *C*-metallated species in solution within the limits of detectability of the ^{13}C NMR method.

H. DEHYDRATED OFFRETITE

In zeolites magnesium normally occurs in six-coordination with oxygen and hydroxyl, though four-, five- and eight-coordinations occur infrequently [19]. Mortier et al. reported [19] the occurrence of three-coordinated magnesium in dehydrated offretite, a rare natural zeolite. A hydrated crystal was dehydrated in a silica capillary for 22 h at 500°C and 10^{-5} Torr before sealing. Diffraction patterns were obtained using MoKα radiation from which structure 36 was deduced. Magnesium occupies the center of a single six-ring where it is bonded to three oxygens at 0.208(1) nm. The six-ring is very distorted to accomodate this short distance and the other three oxygens are displaced outwards to 0.288(2) nm. Some weak bonding may occur to these three oxygens but the strong disparity in the distances implies that the magnesium is effectively three-coordinated. The predicted Mg—O distance for three-coordination is less than 0.19 nm. The unusual coordination of dehydrated offretite results from the spatial restrictions posed by the topology and geometry of the aluminosilicate framework. The four-rings cannot



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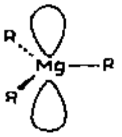
accomodate the magnesium ion because of electrostatic repulsion from the Al, Si ions and the center of a six-ring offers the best of a set of bad options. Because of spatial restrictions the six-ring cannot pucker sufficiently to yield a near octahedral coordination, though it can pucker to give triangular coordination. Thus the magnesium ion which would have had a reasonable coordination in the hydrated zeolite becomes forced into an unusual coordination according to the authors' explanation. They suggest that since the magnesium ion of dehydrated offretite should have a strong electrostatic field around it that sorbed molecules should be strongly attracted to form a complex and perhaps catalytic properties would result. It should be noted that this is apparently the only published X-ray diffraction study furnishing evidence for three-coordinate magnesium in a solid substance.

I. BONDING AND STRUCTURES

The electronic structure of the magnesium atom is $1s^2 2s^2 2p^6 3s^2$. For the formation of compounds containing four-coordinate magnesium six electrons are needed to complete the electron octet in the form of sp^3 hybrid orbitals as seen in compounds for which structures have been determined.

For three coordinate magnesium, assuming donation of four electrons to the magnesium atom and assuming equivalent ligands as in R_3Mg, the preferred type of bonding would be sp^2 (37). The geometry would be trigonal planar [117], with Mg—R bonds in the same plane, R—M—R angles equal to 120° and a vacant $3p$ orbital above and below this plane. There are no reported examples of a compound of this type. However, the only reported example of a compound having been prepared apparently having 120° angles because of geometrical constraints imposed by the ring and "back bonding" is the six-membered ring n-butyl magnesium isopropoxide trimer (22: R = n-Bu, R′ = i-Pr). A possibility that has been suggested [36] for some compounds containing three-coordinate magnesium is back-donation or back-bonding to magnesium from a ligand containing an electron lone-pair (38, 39). Dehydrated offretite in which "back-bonding" of electrons from the three oxygens would also be possible would be similar in that three oxygens are bonded to magnesium. It should be noted that three of the oxygen—magnesium distances were found to be 0.208(1) nm, this relatively short bond distance being in accord with the back-bonding picture. In a compound where one of the ligands is different, $R_2R'Mg$ or all three are different, $RR'R''Mg$, geometry would be expected to be unsymmetrical planar



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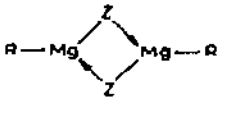
with the bond angles deviating from the ideal 120°. It should be emphasized (as pointed out by the referee) that one cannot consider the sp^2 model and the back-bonding model to be really different. The back-bonded model really means sp^2 plus a π bond (or bonds) and the sp^2 σ-bond framework determines the geometry, on the basis of almost any model including sp^2 hybrid orbitals and the VSEPR rules, a three-coordinated magnesium compound would be expected to have planar trigonal geometry.

In the case of the amide prepared by Coates and Ridley [53] since the two magnesiums are in the four-membered ring (with two nitrogens, two carbons or one nitrogen and one carbon, depending on the correct structure), and the internal ring angle (Z—Mg—Z) must be close to 90°, the R—Mg—Z angles must be approximately 135° (40) assuming planarity of R groups and the ring. The same situation would obtain for the dialkylmagnesium compounds prepared by Glaze and Selman [99], Kamienski and Eastham [100] and Anderson and Wilkinson [106], and also the 4-membered ring structures for the enolates prepared by Fellmann and Dubois [116].



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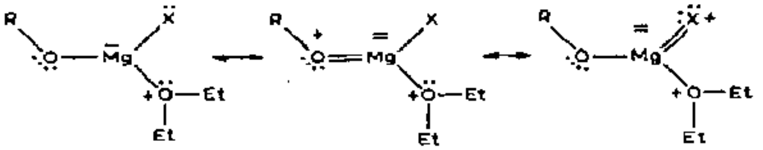

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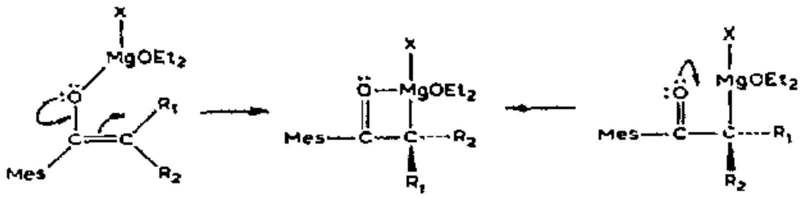
The case of the other magnesium enolates presents a different situation than the preceding ones. In these cases the magnesium is bound to two differently-substituted oxygens and one halogen so that bond angles approximating 120° would be possible (R = organic group). In these cases, back-bonding is also possible, either from alkoxy oxygen (41) and/or the halogen (42) as shown, perhaps as a resonance hybrid of the structures shown. Back-donation of electrons from the ether oxygen would probably not be expected to contribute very much to the resonance hybrid.

Another structural possibility can be approached from the standpoint of either the enolate or keto structures. Starting with the enolate structure (43), π-electrons from the C=C bond can form a σ-bond using the empty orbital of magnesium. A non-bonded electron pair from oxygen can then form a π-bond with carbon. This results in structure 44. Structure 44 can



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also be derived from the keto structure (45) by donation of one of the non-bonded pairs of electrons on oxygen to the empty magnesium orbital.

Although the enolate structure (43) is in accord with the experimental evidence, and seems more probable at present, structure 44 cannot be entirely excluded. Thus, in the case of the ^{1}H NMR data, for example, the two methyl groups substituted on the enolate alkene skeleton are magnetically non-equivalent. For structure 44, they would also be non-equivalent since one methyl group would be on the same side of the ring as the halogen whereas the other would be *cis* to the diethyloxy group. Four-membered rings containing magnesium exist as has been shown for other compounds discussed in this review. Structure 44 would also explain reactions that take place at oxygen (*O*-acylation with benzoyl chloride) or carbon (reaction with benzaldehyde) as discussed previously. A crystal structure determination would definitely decide between the two possibilities suggested.

J. SUMMARY

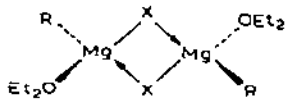
(i) General

In general, the existence of three-coordinate magnesium in compounds has been attributed to steric influences which inhibit or prevent the formation of an additional bond to magnesium. In some cases back-bonding apparently supplies electrons to magnesium.

It is evident that more work needs to be done. In some cases where compounds apparently contain three-coordinate magnesium, more than one structure is possible according to evidence presently available so that structure determinations need to be carried out. Also solid state studies of some of the reported compounds in solution that have been obtained in crystalline form should be carried out. At the present time no crystal structure studies have been reported on any of the compounds for which solution data are available. It would be expected that differences will be found between the structures and conformations of molecules of these compounds in solution and in the solid state. Possible differences in molecular association in solution vs. the solid state relating to three-coordination in magnesium are anticipated by Coates and Ridley [53]. Such differences have been noted with other organometallic compounds in particular with the Grignard reagent, which has been studied most, as a notable example.

(ii) Priority summation

The earliest preparations of compounds which possibly could contain three-coordinate magnesium were the monoetherates $RMgX \cdot R'_2O$, reported by Grignard in his early papers. However, the compounds were incorrectly formulated as quadrivalent oxonium structures and later as a Werner-type complex by Chelintzev. Although an ether-coordinated type structure later emerged from studies on the dietherate, apparently no molecular association studies on solutions of the monoetherate or solid-state crystal structure studies have yet been carried out. On the basis of results reported with other organomagnesium compounds, it is probable that these Grignard monoetherates (if their existence is confirmed) could have structures bridged by means of halogen (46), oxygen (47) or alkyl (48), or a combination of these (49 is



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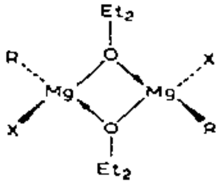

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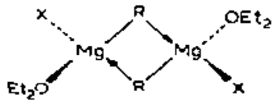

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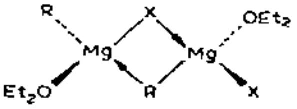

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one example). (*Cis* and *trans* structures are possible; *trans* is shown.) Of these, 46 would probably be more likely on the basis of the order of electron availability of X, O and alkyl based on results from studies on other organometallic compounds.

Chelintzev [85] was apparently the first to prepare organomagnesium halide aminates and to furnish thermochemical evidence for monosolvated species [86]. Ashby [88] confirmed the monosolvated nature of these compounds and determined that they were monomeric in triethylamine solution. In the crystalline state [90] or in benzene solution [89] however, bromine-bridged dimers are formed.

Although no structures were proposed by Glaze and Selman [99] in 1966, it is possible that dimeric n-pentylmagnesium in benzene has an alkyl-bridged structure similar to that proposed later in 1969 for dimeric di-sec-butylmagnesium in cyclopentane by Kamienski and Eastham [100].

In 1967 Coates and Ridley [53] prepared an alkylmagnesium amide by reacting diisopropylmagnesium and diisopropylamine. The ether-free product was dimeric in benzene. The authors preferred a nitrogen-bridged structure over two other possibilities involving carbon-bridging, all containing three-coordinate magnesium.

Kohler et al. [112] in 1935 prepared the first compounds for which there is now evidence [114] for three-coordinate magnesium. These are the *E, Z* isomers of the bromomagnesium monoetherate derivative of 2,2-diphenylethyl 2,4,6-trimethylphenyl ketone. Elemental analyses carried out on these compounds in 1948 by Nesmeyanov et al. [113] showed that they were both monoetherates. Cryoscopic determinations in naphthalene and benzene in 1975 [114] showed the isomers were monomeric, infrared spectra confirmed the enolic nature, and through the ^{1}H NMR spectra on the corresponding enol benzoates, configurations of the corresponding magnesium enolates were assigned.

The only X-ray diffraction study on a compound containing three-coordinate magnesium is dehydrated offretite in a report by Mortier et al. in 1975 [19].

ACKNOWLEDGMENTS

The author expresses appreciation to the Robert A. Welch Foundation of Houston for research grants supporting this work and the work reviewed in this paper and to Baylor University for sabbatical leave during part of which the writing of this review was completed. The author also acknowledges helpful comments from the referee in clarification of the discussion in the section on bonding and structure and to Dr. E.C. Ashby, Georgia Institute of Technology, for his letter and reprint relative to the Grignard triethylamine solvates.

NOTE ADDED IN PROOF

A review of three coordination in metal complexes has just appeared; P.G. Eller, D.C. Bradley, M.B. Hursthouse and D.W. Meek, Coord. Chem. Rev., 24 (1977) 1. It does not, however, include magnesium.

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