Magnesium Bromide–Tetrahydrofuran Complexes: $MgBr_2(C_4H_8O)_2$, $MgBr_2(C_4H_8O)_3$, $MgBr_2(C_4H_8O)_4$, and $MgBr_2(C_4H_8O)_4(H_2O)_2$. A Reagent For the Preparation of Anhydrous Magnesium Phosphodiester Salts

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Abstract: The reaction of magnesium metal with mercuric bromide in anhydrous tetrahydrofuran gives, after removal of mercury, a solution containing two complexes in equilibrium: $MgBr_2(C_4H_8O)_3 + C_4H_8O \rightleftharpoons MgBr_2(C_4H_8O)_4$. The former is obtained as a *microcrystalline* powder at temperatures >30 °C, and the latter as *tetragonal* crystals at temperatures <5 °C. These complexes are in equilibrium with a third one in dichloromethane solution: $MgBr_2(C_4H_8O)_3 \rightleftharpoons MgBr_2(C_4H_8O)_2 + C_4H_8O$; the latter is obtained as *orthorhombic* crystals by addition of hexane to the dichloromethane solution. The three complexes are converted into $MgBr_2(C_4H_8O)_4(H_2O)_2$ (*triclinic*) in THF containing 2 molar equiv of water. All complexes are transformed into $MgBr_2(H_2O)_6$ in aqueous solution. The microcrystalline complex is an excellent reagent for the preparation of anhydrous magnesium phosphodiester salts in dichloromethane solution: $2(R^1O)(R^2O)P(O)OCH_3 + MgBr_2(C_4H_8O)_3 \rightarrow [(R^1O)(R^2O)P(O)O]_2Mg + 2CH_3Br + 3C_4H_8O$. The compositions of the complexes are established by elemental analysis and by ^1H NMR spectrometry in $CDCl_3$ containing dimethylformamide as internal reference. Single-crystal x-ray diffraction analyses of the new orthorhombic and triclinic complexes are presented in a companion paper. The unit cell dimensions of the tetragonal complex agree with those previously reported by Perucaud and LeBihan, and by Schröder and Spandau.

"Magnesium bromide etherate" has been used as reagent for the conversion of epoxides into ketones.[2,3] The reagent was made from magnesium and mercuric bromide in a mixture of diethyl ether and benzene,[2] or from magnesium and 1,2-dibromomethane.[3]

Magnesium bromide has also been made from magnesium and bromine, with or without solvent.[4] This and subsequent studies[4,5] focused on the composition of the magnesium bromide obtained by different procedures; the latter were critically examined by Ashby and Arnott,[6] who reported significant variations in the purity of the products. These authors recommended the magnesium-mercuric bromide reaction in a mixture of diethyl ether and THF,[7] and reported a Mg/Br ratio of 1/1.96 for the white solid, which they obtained after evaporation of the solvents under vacuum.

Schibilla and LeBihan[8] carried out the x-ray diffraction analysis of $MgBr_2[O(C_2H_5)_2]_2$, and reported discrete molecules with four-coordinate magnesium in this very unstable complex. On the other hand, Schröder and Spandau[9] and Pérucaud and LeBihan[10] found discrete molecules, $MgBr_2 \cdot (C_4H_8O)_4$, with six-coordinate magnesium in the tetragonal crystals which they obtained from magnesium and bromine in THF solution.

The present investigation deals with two aspects of magnesium bromide chemistry: (1) a reinvestigation of the reaction of magnesium with mercuric bromide in THF solution to determine if one or more than one type of complex is formed between magnesium bromide and the cyclic ether under different experimental conditions; and (2) a study of the magnesium bromide complexes as potential reagents for the preparation of anhydrous magnesium phosphodiester salts, according to the following reaction:

$$2(R^1O)(R^2O)P(O)OCH_3 + MgBr_2(C_4H_8O)_x \xrightarrow[\text{solvent}]{\text{aprotic}} [(R^1O)(R^2O)P(O)O]_2Mg + 2CH_3Br + xC_4H_8O$$

This paper describes the preparation of four magnesium bromide-THF complexes, and of a number of magnesium phosphodiester salts prepared by the above reaction, utilizing tris(tetrahydrofuran)magnesium bromide, $MgBr_2(C_4H_8O)_3$, as reagent. The following paper[11] describes the x-ray diffraction analysis of two of the three new magnesium bromide-THF complexes, and the confirmation of the formula and the unit cell dimensions of the known[9,10] $MgBr_2(C_4H_8O)_4$ compound.

Few magnesium phosphodiester salts are described in the literature,[12,13] in spite of their obvious relevance to problems associated with polynucleotide and nucleic acid structure and function. Ezra and Collin[12] made magnesium diethyl phosphate by the reaction:

$$2(C_2H_5O)_2P(O)OAg + MgCl_2 \xrightarrow{H_2O} [(C_2H_5O)_2P(O)O]_2Mg + 2AgCl$$

These authors found, in the crystal, magnesium ions coordinated in a nearly regular tetrahedral arrangement to four nonester oxygen atoms from four different phosphates, with each anion bound to two mgnesium ions in a polymeric structure.

Results and Discussion

Preparation of Magnesium Bromide–Tetrahydrofuran Complexes. The reaction of an excess of magnesium with a THF solution of mercuric bromide affords, after removal of the solid phase, a clear solution from which thin plates separate upon cooling at 5 °C. The unit cell dimensions of these crystals agree with those reported by German[9] and French[10] investigators for the *tetragonal* crystals, which contain the formula unit $MgBr_2(C_4H_8O)_4$ (**1**). This formula can be confirmed by ^1H NMR measurements in deuteriochloroform solution containing DMF[7] as internal reference (see Experimental Section).

A different complex is obtained when the THF solution obtained from the magnesium-mercuric bromide reaction is concentrated at 30 °C until a solid phase appears. The compound is obtained as a powder, with the composition[14] $MgBr_2(C_4H_8O)_3$ (**2**) according to the elemental analysis shown in Table I and the ^1H NMR measurements. X-ray

Table I. Elemental Analyses and Spectral Data of Magnesium Bromide–Tetrahydrofuran Complexes and of Anhydrous Magnesium Phosphodiester Salts

Compd no.	Formula	Main NMR signals^{a}		Elemental composition (FW)	% calcd				% found			
		^{31}P, ppm	^{1}H, ppm		C	H	Mg	X	C	H	Mg	X
2	$MgBr_2(C_4H_8O)_3$		8.00, 5.90^{b}	$C_{12}H_{24}O_3MgBr_2$ (400)	36.0	6.0	6.1	39.9^{c}	35.9	6.1	6.2	40.0
3	$MgBr_2(C_4H_8O)_4(H_2O)_2$		8.14, 6.22^{d}	$C_{16}H_{36}O_6MgBr_2$ (508)	37.8	7.1	4.7	31.5	38.5	7.0		
4	$MgBr_2(C_4H_8O)_2$		8.14, 6.22^{d}	$C_8H_{16}O_2MgBr_2$ (328)	29.3	4.9	7.3	48.8	29.0	4.8	7.5	48.5
	$[(R^1O)(R^2O)P(O)O]_2Mg^{e}$ $(R^1; R^2)$											
11	CH_3; CH_3	−2.8^{f}	6.40^{f}	$C_4H_{12}O_8P_2Mg$ (274)	17.5	4.4	8.8	22.6^{g}	17.2	4.5	8.5	22.4
12	$CH_3(CH_2)_6CH_2$; $CH_3(CH_2)_6CH_2$	5.8^{b}	6.20^{h}	$C_{32}H_{68}O_8P_2Mg$ (666)	57.7	10.2	3.6	9.3	57.5	10.2	3.5	9.4
13	C_6H_5; CH_3		6.35^{f}	$C_{14}H_{16}O_8P_2Mg$ (398)	42.2	4.0	6.0	15.6	42.0	4.0	6.0	15.5
17	p-$NO_2C_6H_4$; CH_3; $CH_3NC_3H_3N^{i}$	9.6^{j}	6.42, 6.29^{k}	$C_{18}H_{20}O_{12}N_4P_2Mg$ (570)	37.9	3.5	4.2		38.0	3.6	4.1	
15	$CH_2{=}CCO_2CH_3$; CH_3		6.42, 6.20^{f}	$C_{10}H_{16}O_{12}P_2Mg$ (414)	28.9	3.8	5.8	14.9	27.6	3.9	5.2	13.8
16	$CH_3C{=}CCH_3$	−13.9^{f,l}	8.15^{h}	$C_8H_{12}O_8P_2Mg$ (322)	29.8	3.7			29.6	4.2		

[a] ^{1}H NMR signals in parts per million from $Me_4Si = 10$ (τ). ^{31}P NMR signals in parts per million from $H_3PO_4 = 0$. [b] In $CDCl_3$. [c] X = Br. [d] In $CDCl_3$ + DMF. The water present in **3** gives a signal at $\tau \sim 4.90$ ppm. [e] Yields (%): **11**, 71; **12**, 61; **13**, 87; **14**, 90; **15**, 70; **16**, 97. [f] In D_2O. [g] X = P. [h] In $CDCl_3$ + a drop of Me_2SO-d_6. [i] Complex with N-methylimidazole; N, calcd 9.6; found 9.7%. [j] In $CDCl_3$ + N-methylimidazole. [k] In 90% Me_2SO-d_6 + 10% $CDCl_3$. [l] −10.0 (CD_3OD), −6.9 (90% Me_2SO-d_6 + 10% $CDCl_3$).

Table II. Solubility of Complexes of Magnesium Bromide^{a}

Solvent	$MgBr_2$-$(THF)_3$ (**2**)	$MgBr_2$-$(THF)_4$-$(H_2O)_2$ (**3**)	$MgBr_2$-$(THF)_2$ (**4**)	$MgBr_2$-$(H_2O)_6$^{b}
Dichloromethane	3.0	i^{c}	i	i
Chloroform-d^{d}	1.5	i	i	i
Carbon tetrachloride	i	i	i	i
Tetrahydrofuran	0.2	i	0.1	i
Diethyl ether	0.02	i	0.007	i
1,2-Dimethoxyethane	0.008	i	0.005	i
Benzene	0.008	i	i	i
Ethylene glycol	1.0	1.8^{e}	0.8	v.s.^{e}

[a] Molarity of the solutions obtained when mixtures of the complex and the solvent are stirred for 8–12 h at 25 °C. [b] Fischer Scientific Co. Reagent Grade. [c] i = solubility < 0.001 M. [d] The solubility of the complexes **2–4** in chloroform-d increases significantly upon addition of a few vol % of Me_2SO-d_6 or DMF. [e] The composition of the solvent is altered by the water of hydration; v.s. = very soluble.

powder photographs[11] reveal a high degree of crystallinity in this solid, although no single crystals of it have, so far, been obtained. A THF solution of powder **2** deposits tetragonal crystals **1** upon cooling at 5 °C, provided that the THF is strictly anhydrous and that the appropriate concentration is achieved.

A third complex is obtained when limited amounts of water are introduced into a THF solution of powder **2.** The translucent thick plates that crystallize at 20 °C belong to the *triclinic* system and have the composition $MgBr_2(C_4H_8O)_4(H_2O)_2$ (**3**) according to elemental analysis and ^{1}H NMR spectrometry, confirmed by x-ray crystallography.[14]

A fourth complex is obtained when a dichloromethane solution of powder **2** is diluted with hexane at 20 °C and allowed to crystallize at 5 °C. The resulting needles belong to the *orthorhombic* system, and have the composition $MgBr_2(C_4H_8O)_2$ (**4**) from elemental analysis, ^{1}H NMR spectrometry, and x-ray diffraction analysis.[14] The addition of benzene or of diethyl ether to the dichloromethane solution of powder **2** leads also to orthorhombic **4.**

A solution of orthorhombic **4** in THF deposits triclinic **3** upon addition of small amounts of water. All the complexes, **1–4,** are converted into hexaaquomagnesium(II) bromide when dissolved in water.

The tetragonal crystals **1** are relatively unstable and can be transformed into powder **2** in 1 h at 25 °C and 1 mm. However, these conditions do not significantly affect the composition of the other complexes **2–4.**

The solubility of complexes **2–4** in several organic solvents is given in Table II. Powder **2** has the highest solubility in all the aprotic solvents. Differences of this type,[15] with the exception of the data pertaining to THF, can be interpreted as simply reflecting differences in intermolecular forces in the respective crystals;[16] however, two points are worth noting. (1) Orthorhombic **4** does not crystallize out of solutions of powder **2** in the aprotic solvents, in spite of the fact that crystals of **4** are quite insoluble in those solvents. This could mean that the following equilibrium lies far to the left in these media:

$$MgBr_2(C_4H_8O)_3 \rightleftharpoons MgBr_2(C_4H_8O)_2 + C_4H_8O$$

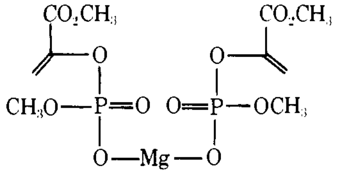
That this equilibrium does exist is indicated by the appearance of orthorhombic crystals **4** when hexane, benzene, or diethyl ether are added to a dichloromethane solution of powder **2.** (2) Triclinic **3** is even less soluble than orthorhombic **4** in diethyl ether and 1,2-dimethoxyethane. The aquo complex **3** has significant solubility in the protic solvent ethylene glycol, and the anhydrous complexes **2** and **4** are also quite soluble in the glycol.

The solubility data in THF are interesting. The slight difference in solubility between powder **2** and orthorhombic **4** is not regarded as significant; in fact, common species must exist in those solutions, since the addition of a limited amount of water to the THF solutions causes precipitation of triclinic crystals **3** in both cases. On the other hand, triclinic **3** is significantly less soluble than powder **2** in THF, and this suggests that the low dielectric THF cannot bring any of **3** into solution, or that if it does, the composition of the complex remains as it was in the crystal of **3,** i.e., there is no substitution of water ligands by THF ligands which are present in large excess. As expected, $MgBr_2(H_2O)_6$ is not appreciably soluble in any of the aprotic organic solvents.

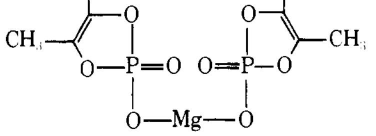
The ^{1}H NMR spectrum of a $CDCl_3$ solution of powder **2** is consistent with the conclusion that the complex $MgBr_2(C_4H_8O)_3$ has predominantly this composition in the organic solvent, as well as the solid state. The separation between the centers of the multiplets due to the α and β protons in the *bound* THF is 124 Hz (at 60 MHz). Pure THF in $CDCl_3$, at comparable concentration, exhibits a separation of 112 Hz. The 12-Hz difference results from a larger low-field displacement of the α protons (16 Hz) vs. the β protons (4 Hz) when THF becomes complexed to magnesium. The addition of several molar equivalents of DMF to the $CDCl_3$ solution of the complex, **2**, restores the 112-Hz separation between the THF signals, suggesting a facile displacement of THF by DMF in the magnesium coordination sphere.

Tetragonal **1**, triclinic **3**, and orthorhombic **4** are not sufficiently soluble in pure $CDCl_3$ for ^1H NMR determination. The three complexes dissolve readily upon addition of a few molar equivalents of DMF to the $CDCl_3$ suspension. This allows the determination of the composition of these complexes (as well as of **2**), since the six protons of DMF serve as a convenient internal reference with respect to the THF protons (see Experimental Section). However, this technique cannot be used to study the state of the various complexes in solution, since the DMF rapidly displaces the THF ligands from the magnesium.

Preparation of Anhydrous Magnesium Phosphodiester Salts by Means of Tris(tetrahydrofuran)magnesium Bromide (2). The powder **2** is a convenient reagent for the preparation of anhydrous magnesium phosphodiesters according to the reaction suggested in the introduction. The reagent itself is easily made from mercuric bromide in 90% yield, is relatively stable, and has satisfactory solubility in dichloromethane and THF. The reaction gives a volatile by-product, CH_3Br, and proceeds without apparent side reactions. Several magnesium phosphates, **11-16**, made from the corresponding phosphotriesters, **5-10**, are shown in Table I. Of particular interest are the salts of phosphoenolpyruvate (**15**) and of the enediol cyclic phosphate (**16**).

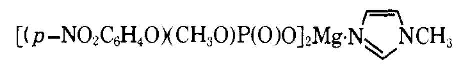


15



16

The anhydrous magnesium phosphodiester salts do not form relatively stable tetrahydrofuran or diethyl ether complexes of the type formed by magnesium bromide. This difference may be related to the presence in the phosphate group of oxygen functions capable of fulfilling the coordination of the magnesium atom.[12,13] The ability of the magnesium phosphates to form complexes with suitable donors is shown by the preparation of the relatively stable *N*-methylimidazole complex (**17**) of magnesium *p*-nitrophenylmethyl phosphate (**14**).

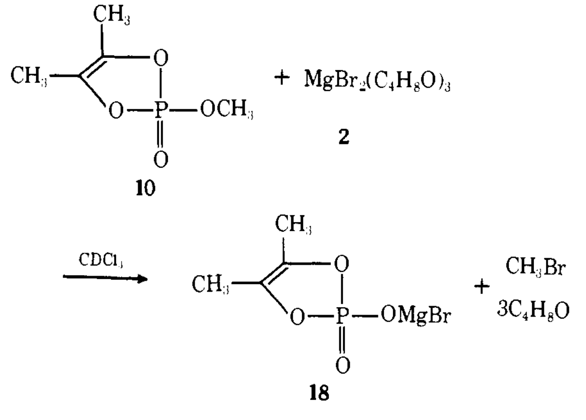


$$[(p\text{-}NO_2C_6H_4O)(CH_3O)P(O)O]_2Mg\cdot N\;\;NCH_3$$

17

The magnesium phosphates **11-16** are relatively soluble in water, methanol, and Me_2SO. The dioctyl salt **12** is appreciably soluble in dichloromethane, chloroform-*d*, THF, diethyl ether, and benzene. The cyclic salt **16**, and the phenyl methyl salt **13**, have some detectable solubility in the chlorocarbons and in THF, but not in the other solvents mentioned. The rest of the salts do not show appreciable solubility in the organic solvents. None of the salts is appreciably soluble in acetonitrile.

The reaction of the esters, **5-10**, with the $MgBr_2(C_4H_8O)_3$ complex **2** seems to proceed in two distinct stages: (1) a nucleophilic attack by the Br^- of **2** on the methyl group of the ester to give methyl bromide and the bromomagnesium salt (**18**) as illustrated with the cyclic ester **10**;[17] and (2) a slower attack by the Br^- of **18** on a second molecule of the ester **10** to give more methyl bromide and the magnesium phosphodiester salt **16**. This conclusion follows from observations of the ^1H NMR spectra obtained when equal volumes of 0.4 and 0.2 M $CDCl_3$ solutions of the ester **10** and the complex **2** are mixed at 25 °C. Within ca. 7 min, under these conditions, equimolar concentrations of methyl bromide and of unreacted ester **10** are observed. Virtually all the ester **10** is consumed within 1.5 h, at which point 2 molar equiv of methyl bromide is produced, in addition to the product **16**. The disproportionation of the intermediate **18** is a conceivable reaction, but its intervention in the formation of the final product was not investigated.



(1)

$$2(\mathbf{18}) \rightarrow \mathbf{16} + MgBr_2 \qquad (2)$$

Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and are given in Table I. The magnesium bromide complexes and the magnesium phosphodiester salts are hygroscopic; they can be handled under a blanket of Ar or N_2, or preferably by drybox techniques. All solvents were strictly anhydrous.

Preparation of Tris(tetrahydrofuran)magnesium Bromide (2; microcrystalline). Magnesium shavings (7.9 g, 0.3 g-atom) were added to a mixture of mercuric bromide (20 g, 0.055 mol) and freshly distilled THF (400 mL). The mixture was kept for 5 h at reflux, and for 12 h at 25 °C. The clear supernatant solution was decanted from the solid phase. The solution was concentrated to ca. 200 mL in a rotoevaporator *at 30 °C (30 mm)*, which resulted in the formation of a copious crop of fine, white crystals. After several hours *at 20 °C*, the crystals were collected in a sintered glass funnel, with protection from moisture, and were dried in a current of Ar to constant weight: 19 g, or 90% of the theory based on $MgBr_2(C_4H_8O)_3$ (**2**). This composition was confirmed by elemental analysis and ^1H NMR spectrometry. X-ray powder photographs[11] revealed a high degree of crystallinity in the powder. The complex **2** did not lose THF after 30 min at 20 °C (1 mm). It can be stored for several days in a vacuum desiccator, over P_2O_5.

Preparation of Tetrakis(tetrahydrofuran)magnesium Bromide (1; tetragonal). (a) From Microcrystalline $MgBr_2(C_4H_8O)_3$ (2). The powder (**2**, 1 g) was dissolved in *anhydrous THF* (75 mL) at 45 °C. The clear solution did not deposit crystals at 20 °C. After 6 days at 5 °C, large, thin plates had formed, and were collected and dried in a current of Ar. The unit cell dimensions[11] agreed with those previously reported[9,10] for the tetragonal crystals of $MgBr_2(C_4H_8O)_4$ (**1**). The composition was verified by ^1H NMR spectrometry.

(b) Directly from The Reaction: $Mg^0 + HgBr_2$. The reaction was carried out as described above, except that the final solution was not concentrated, but was kept several days *at 5 °C*. The large, thin plates characteristic of the tetragonal complex **1** were collected and analyzed by ^1H NMR spectrometry.

(c) Directly from The Reaction: $Mg^0 + Br_2$. The reaction of bromine with magnesium was carried out in THF as described.[4,10] The white powder was dissolved in warm THF and the solution was kept several days at 5 °C. The thin plates which separated had the same appearance as those obtained by a similar procedure, but from the $Mg^0 + HgBr_2$ reaction.

Preparation of Diaquotetrakis(tetrahydrofuran)magnesium Bromide (3; triclinic). (a) From Microcrystalline $MgBr_2(C_4H_8O)_3$ (2). The powder **2** was dissolved, with gentle warming, in THF containing about 2-3 molar equiv of water. The concentration was adjusted so as to promote a very slow rate of crystallization at 20 °C, which produced translucent small thick plates suitable for single-crystal x-ray diffraction analyses;[11] $\rho_{obsd} = 1.426 g cm^{-1}$ by flotation in carbon tetrachloride-hexane. The crystals for x-ray analysis were immediately sealed into a capillary. The crystals for elemental analysis, and for composition determination by ^1H NMR spectrometry (see below), were dried at 20 °C in a current of Ar. Drying for 1 h at 20 °C (1 mm) did not change the composition of the complex within the precision of the spectrometric analysis.

(b) From Orthorhombic $MgBr_2(C_4H_8O)_2$ (4). A solution of orthorhombic crystals **4** in wet THF gave triclinic crystals **3**, on standing at 20 °C and finally at 5 °C, according to the NMR spectrometric analysis and the change in crystal habit.

Preparation of Bis(tetrahydrofuran)magnesium Bromide (4; orthorhombic). (a) From Microcrystalline $MgBr_2(C_4H_8O)_3$ (2). The powder (**2**, 400 mg) was dissolved in dichloromethane (2 mL) at 20 °C. The solution was diluted with hexane (0.6 mL) and kept several hours at 20 °C and several days at 5 °C. These conditions promoted the formation of needles suitable for single-crystal x-ray diffraction analysis;[11] $\rho_{obsd} = 1.99 g cm^{-3}$ by flotation in carbon tetrachloride-bromoform (rapid determination). The crystals for x-ray analysis were immediately sealed in a capillary. The samples for elemental analysis, and for the composition determination by ^1H NMR, were dried at 20 °C in a current of Ar. The composition of the complex did not change appreciably after 1 h at 20 °C (1 mm).

The addition of benzene or of diethyl ether to the dichloromethane solution of the powder **2** caused the appearance of the orthorhombic crystals **4**. This was verified by unit cell determination.

Determination of Complex Composition by ^1H NMR Spectrometry. A sample (ca. 50 mg) of the compound, **1-4**, previously dried in a current of Ar, was weighed into the NMR tube. A solution (ca. 1 mL) of $CDCl_3$ containing a weighed amount of the reference compound, DMF (ca. 35 mg), was introduced, and the tube was shaken to obtain a clear solution. The ^1H NMR spectrum was recorded at 60 MHz. The integrated intensities of the six DMF and the eight THF protons were normalized, and this DMF/THF intensity ratio was compared with the DMF/THF molar ratios calculated from the weights of DMF and of sample, assuming various compositions for the latter, $MgBr_2(C_4H_8O)_x$, $x = 1-4$, using the formula: $x \times$ wt/(mol wt). Agreements between observed and calculated ratios of 3-5% were obtained by this procedure for the complexes **1-4**.

Conversion of Tetrahydrofuran-Containing Complexes of $MgBr_2$ (2, 3) into Hexaaquomagnesium(II) Bromide. The powder (**2**, 300 mg) was dissolved in water (1.2 mL). THF was added, gradually, to the aqueous solution, which remained clear up to ca. 10 mL of THF, but deposited crystals when the THF volume reached 17 mL. The crystals were filtered and dried to constant weight; they proved to be $MgBr_2(H_2O)_6$ according to the ^1H NMR in 90% Me_2SO-d_6 + 10% $CDCl_3$, in the presence of DMF added for calibration purposes. No THF signals were present, and the water signal was noted at ca. τ 6.20 ppm.

The triclinic crystals **3** were dissolved in water. The water was evaporated at 0.2 mm and the resulting solid was dissolved in Me_2SO-d_6 (90%) + $CDCl_3$ (10%) containing DMF; the ^1H NMR spectrum confirmed the formation of $MgBr_2(H_2O)_6$.

Preparation of Phosphotriesters. Phenyldimethyl phosphate[18] (**7**), *p*-nitrophenyldimethyl phosphate[18] (**8**), dimethyl(1-carbomethoxyethenyl) phosphate (**10**, trimethyl phosphoenolpyruvate),[19] and methyl(1,2-dimethylethenylene) phosphate[17] (**9**), were made by published procedures.

Dioctylmethyl Phosphate (8). (By general procedure 2B in ref 20.) A dichloromethane (40 mL) solution of imidazole (3.76 g, 55 mmol) was added to di(1,2-dimethylethenylene) pyrophosphate[21] (7.80 g, 27.5 mmol), and the solution was stirred for 15 min (20 °C). *n*-Octyl alcohol (7.18 g, 55 mmol) in dichloromethane (20 mL) solution was added in one portion, with stirring, at 20 °C. The solution was stirred overnight, was diluted with dichloromethane (100 mL), and was extracted with 5% sodium carbonate (three times), 5% HCl (twice), and water (once). The solution was dried (Na_2SO_4) and evaporated to give virtually pure dioctyl(1-methylacetonyl) phosphate (10.5 g, 94% of the theory). A solution of this triester (8.6 g, 21 mmol) in acetonitrile (75 mL) and water (150 mL) was treated with diisopropylethylamine (2 molar equiv; triethylamine can be used). The solution was stirred at 70 °C for 10 h, and at 20 °C for 6 h. The acetonitrile was evaporated under reduced pressure and the aqueous solution was treated with sodium carbonate (4.5 g) and extracted with dichloromethane (three 40-mL portions). The *organic extract* was dried (Na_2SO_4) and evaporated (30 °C (30 mm)) to yield the salt, $(RO)_2P(O)O^-R_3NH^+$, due to the hydrophobic nature of the alkyl chains. The salt was dissolved in water (150 mL), acidified with 5% HCl, and reextracted with dichloromethane (three 50-mL portions). The dried organic extract afforded dioctylhydrogen phosphate, mp 28-30 °C, in 93% of the theory (6.3 g, lit.[22] mp 29-30 °C, obtained by a different procedure). The acid was converted into dioctylmethyl phosphate[23] by diazomethane in diethyl ether.

General Procedure for the Preparation of Anhydrous Magnesium Phosphodiester Salts, 11-16, by Means of Tris(tetrahydrofuran)magnesium Bromide (2). (a) In Dichloromethane. The phosphotriester, **5-10** (2 molar equiv), neat or dissolved in dichloromethane, was mixed with 1 molar equiv of the complex **2** dissolved in dichloromethane. The 0.2-0.25 M solution was refluxed overnight. The relative rates of reaction were: **10** ~ **8** > **7** > **9**, **6**, **5**, and under these conditions, the reaction of **10** was virtually complete in 2 h. The resulting clear or gelatinous mixture (depending on the ester) was evaporated (rotoevaporator, 30 °C (30 mm)), and the residue was extracted, successively, with small portions of diethyl ether, benzene, and diethyl ether. The residual powder was dried for 1 h at 25 °C (0.1 mm) and submitted for elemental analysis. The salts were stored in a desiccator over P_2O_5.

(b) In THF. Several salts were also prepared as in (a), but in 0.2 M THF solution.

(c) In $CDCl_3$. This solvent was used to follow the progress of the reactions by ^1H NMR measurements.

Complex of Magnesium *p*-Nitrophenylmethyl Phosphate (14) with Imidazole. The salt **14** (800 mg) was suspended in hot THF (150 mL) and treated with *N*-methylimidazole (5 mL) to give a clear solution. The solution was kept overnight at 25 °C, and the resulting solid was filtered, washed with THF (two 10-mL portions), and dried for 2 h at 50 °C (0.1 mm) and 2 h at 25 °C (0.1 mm). The yellow powder had elemental analysis and NMR spectra which correspond to those of the 1:1 salt-*N*-methylimidazole complex (**17**).

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(15) The mixture of excess crystals and solvent was stirred until saturation of the solution was achieved; the undissolved crystals were filtered off, and the solution was evaporated. A significant degree of supersaturation can be produced if successive portions of the crystals are added to a well stirred solution.

(16) Dielectric constants at 20 °C: CH_2Cl_2, 9; $CHCl_3$, 4.8; CCl_4, 2.2; tetrahydrofuran, 1 6; diethyl ether, 4.3; ethylene glycol, 38 (25 °C); benzene, 2.8; H_2O, 78 (25 °C) [*Natl. Bur. Stand. (U.S.), Circ.*, **No. 514** (1951); **No. 537** (1953)].

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Crystal and Molecular Structure of Magnesium Bromide–Tetrahydrofuran Complexes: $MgBr_2(C_4H_8O)_2$, Orthorhombic, and $MgBr_2(C_4H_8O)_4(H_2O)_2$, Triclinic

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Abstract: The structure of the magnesium bromide–tetrahydrofuran complex, $MgBr_2(C_4H_8O)_4(H_2O)_2$, has been determined by single-crystal x-ray diffraction. The crystals are *triclinic*, space group $P\bar{1}$, $a = 7.77\ (\pm 0.01)$, $b = 9.26\ (\pm 0.01)$, $c = 9.27\ (\pm 0.01)$ Å, $\alpha = 84.9\ (\pm 0.03)$, $\beta = 71.2\ (\pm 0.03)$, $\gamma = 69.1\ (\pm 0.03)°$, $Z = 1$, $\rho_{calcd} = 1.44$ g cm^{-3}, $\rho_{obsd} = 1.43$ g cm^{-3}. The structure of $MgBr_2(C_4H_8O)_2$ has also been determined. The crystals are *orthorhombic*, space group $P2nn$, $a = 4.01\ (\pm 0.01)$, $b = 7.52\ (\pm 0.01)$, $c = 18.20\ (\pm 0.01)$ Å, $Z = 2$, $\rho_{calcd} = 1.99$ g cm^{-3}, $\rho_{obsd} = 1.99$ g cm^{-3}. Intensity data were collected on a computer controlled CAD4 automatic diffractometer; 2050 and 626 independent reflections were collected using (θ–2θ) scan, with a scan width of 1.0°, for the trinclinic and orthorhombic crystals, respectively. The structures were solved by Patterson methods and refined to final R factors of 7.9% (triclinic, 2043 reflections), and 8.6% (orthorhombic, 618 reflections), by least-squares methods. The structure of diaquotetrakis(tetrahydrofuran)magnesium bromide consists of independent molecules with regular octahedral six-coordinate magnesium: two trans water molecules, Mg–O = 2.042 Å, and two pairs of trans THF molecules, Mg–O = 2.117 and 2.164 Å, respectively; the bromine atoms are in the outer sphere, Mg–Br = 4.651 Å. The structure of bis(tetrahydrofuran)magnesium bromide is polymeric with distorted octahedral six-coordinate magnesium: two trans THF molecules, Mg–O = 2.126 Å, two cis bromine atoms from the same formula unit, Mg–Br = 2.633 Å, and two cis bridging bromine atoms from an adjacent formula unit, Mg···Br = 2.799 Å. A third complex, $MgBr_2(C_4H_8O)_3$, which could have trigonal bipyramidal five-coordinate magnesium, has been isolated only as a microcrystalline powder. A *tetragonal* complex, $MgBr_2(C_4H_8O)_4$, has been reported by Pérucaud and LeBihan and by Schröder and Spandau. The interconversions among these complexes in aprotic solvents are discussed as examples of elimination and substitution reactions. All the complexes easily form $MgBr_2(H_2O)_6$ in water.

Much of the research on the structure of magnesium compounds, as revealed by single-crystal x-ray diffraction techniques, has been motivated by the problem of the constitution of the Grignard reagent.[2] The literature on this subject was reviewed by Toney and Stucky,[3] in connection with their study of the product of the reaction of ethyl chloride with magnesium in tetrahydrofuran (THF). These authors described a tetrameric Grignard reagent, $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$, consisting of two $MgCl_2(C_4H_8O)_2$ units associated with two $C_2H_5MgCl(C_4H_8O)$ units in such a way as to allow the six coordination of the former magnesium atoms and the five coordination of the latter magnesium atoms, with two- and three-coordinate chlorine atoms functioning as bridges. This beautiful structure brings out one of the interesting features of magnesium chemistry, namely, the ability of the metal to adjust its coordination number according to the demands of a particular constitution. Vallino[4] reported trigonal bipyramidal five coordination for the complex $CH_3MgBr(C_4H_8O)_3$. Moseley and Shearer[5] found four coordination for the magnesium in the dimer $[(CH_3)_3COMgBrO(C_2H_5)_2]_2$. Manning and co-workers[6] ascribed five coordination to the metal in the dimer $[(C_6H_5)_2NMgBr(C_4H_8O)]_2$.

In other types of magnesium compounds, six coordination prevails, as in diaquobis(acetylacetonato)magnesium(II),[7] and in a related tris(hexafluoroacetylacetonate) salt.[8] Other significant aspects of the crystal and molecular structure of magnesium compounds have been discussed in previous papers.[9-13]

This investigation focused on the structure of complexes of magnesium bromide with THF. In a previous paper[14] we described the isolation of four complexes with formulas $MgBr_2(C_4H_8O)_4$ (**1**), $MgBr_2(C_4H_8O)_3$ (**2**), $MgBr_2(C_4H_8O)_4(H_2O)_2$ (**3**), and $MgBr_2(C_4H_8O)_2$ (**4**) from the reaction of magnesium with mercuric bromide in THF solution, under various experimental conditions. Complex **1** was obtained as tetragonal crystals, which proved to have the same unit cell dimensions as those reported by Schröder and Spandau[15] and by Pérucaud and LeBihan.[16] Complex **2** has been obtained only as a microcrystalline powder; it has a remarkable solubility in aprotic solvents such as dichloromethane, and constitutes a new reagent to make *anhydrous* magnesium phosphodiester salts by the reaction: $(R^1O)(R^2O)P(O)OCH_3 + MgBr_2(C_4H_8O)_3 \rightarrow [(R^1O)(R^2O)P(O)O]_2Mg + 2CH_3Br + 3C_4H_8O$.

The other two complexes in this series, **3** and **4**, were obtained as single crystals of excellent quality for x-ray diffraction analyses. The results of such a study are described in this paper.

Experimental Section

The samples of diaquotetrakis(tetrahydrofuran)magnesium bromide (**3**, triclinic), and bis(tetrahydrofuran)magnesium bromide (**4**,

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