A Simple Method for Preparing Magnesium Porphyrins

Jonathan S. Lindsey* and Jeffrey N. Woodford

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

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The synthesis of magnesium tetraarylporphyrins has been investigated using magnesium halides in noncoordinating solvents with hindered amine bases. The rate of reaction increases in the series $MgCl_2 \ll MgBr_2 < MgBr_2{\cdot}O(Et)_2 < MgI_2$. Considerable latitude exists in selecting among magnesium reagents ($MgBr_2$, $MgBr_2{\cdot}O(Et)_2$, MgI_2), solvents (toluene, CH_2Cl_2, $CHCl_3$), and bases (triethylamine, diisopropylethylamine, 2,2,6,6-tetramethylpiperidine) for efficient metalation of tetraphenylporphyrin at room temperature. Thus treatment of a toluene, CH_2Cl_2, or $CHCl_3$ solution of tetraphenylporphyrin with excess $MgBr_2$, $MgBr_2{\cdot}O(Et)_2$, or MgI_2 and triethylamine at room temperature quantitatively affords the magnesium chelate in <10 min. Tetramesitylporphyrin is converted to the magnesium chelate with MgI_2 and diisopropylethylamine in CH_2Cl_2 at room temperature in 10 min or by reaction with $MgBr_2{\cdot}O(Et)_2$ and triethylamine in toluene at 60 °C for 1 h. [Tetrakis(2,6-dimethoxyphenyl)porphinato]magnesium(II) was formed in similar fashion. The reaction conditions are compatible with porphyrins bearing (trimethylsilyl)ethynyl groups, and the reactions can be performed in the presence of zinc tetraphenylporphyrin without transmetalation. This approach is fundamentally distinct from that with DMF−$MgCl_2$, which is designed to achieve high mutual solubility of the metal ion and free base porphyrin at elevated temperature. The facile magnesium insertion achieved with $MgBr_2$, $MgBr_2{\cdot}O(Et)_2$, or MgI_2 at room temperature is attributed to the lability of their ligands, their partial organic solubility, and the limited stability of their crystal lattices relative to the porphyrin magnesium chelate. A noncoordinating milieu is essential to avoid forming octahedral complexes of magnesium that are more stable than the magnesium porphyrin. The ability to form magnesium tetraarylporphyrins under gentle conditions enables biomimetic studies where zinc porphyrins have previously been used.

Introduction

Chlorophyll and bacteriochlorophyll contain magnesium as their centrally-coordinated metal. In spite of the wide natural abundance of these compounds, the laboratory insertion of magnesium into porphyrinic ligands has proved surprisingly difficult. Numerous methods have been developed (Table 1).[1−26] Seely's succinct statement, "Magnesium is easy to remove from the porphyrin ring but hard to replace" summarized a half-century of metalation efforts with Grignard reagents or with magnesium complexes at elevated temperatures.[27] The hindered reagent (2,6-di-*tert*-butyl-4-methylphenoxy)magnesium iodide has been employed for metalation of pheophytin and bacteriopheophytin under mild conditions.[17−19] This reagent has found wide application but must be prepared immediately prior to use due to its limited shelf life.

Most of the methods shown in Table 1 were developed for the preparation of magnesium chelates of naturally-occurring porphyrins. *meso*-Tetraphenylporphyrin (TPP) has been converted to the magnesium chelate by a variety of these methods, but the most popular method remains the use of $MgCl_2$ in refluxing DMF developed by Adler *et al.*[14] Relatively few *meso*-tetraarylporphyrins have been converted to their magnesium chelates, and the syntheses of these have generally employed Grignard reagents or $MgCl_2$ in refluxing DMF.[28−40]

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Table 1. Preparative Methods for Inserting Magnesium into Porphyrinic Ligands[a]

reagent	solvent	temp	ref	applications to *meso*-porphyrins[f]
MgO + KOH	methanol	180−220 °C	Willstätter[1]	
CH_3MgI	diethyl ether	25 °C	Willstätter[1]	TPP,[28,29] TPC,[28] A,[29] B,[29] C[29]
$4\text{-}(CH_3)_2NC_6H_4MgI$	diethyl ether	35 °C	Noack[2]	
$MgBr_2$	pyridine	150−160 °C	Fischer[3]	
PrOMgBr[b]	diethyl ether + 1-propanol	heat[e]	Fischer[4]	
EtOMgBr[b]	pyridine + ethanol	heat[e]	Fischer[5]	
MeOMgBr[b]	pyridine + methanol	heat[e]	Fischer[6]	
PrOMgBr[b]	1-propanol	70−75 °C	Granick[7]	TPC[30]
$Mg(OAc)_2{\cdot}4H_2O$ + KOH	methanol + pyridine	170 °C	Rothemund[8]	TPP
Mg(viologen)$_2$	pyridine	115 °C	Wei[9]	TPC[31]
Mg(4,4′-dipyridyl)$_2$	pyridine	115 °C	Wei[9]	
$MgI_2(pyridine)_6$	pyridine	115 °C	Wei[9]	TPP[32]
$Mg(OC_6H_5)_2$	phenol	100 °C	Corwin[10]	
$Mg(ClO_4)_2$	pyridine or 1-propanol	115 or 97 °C	Baum[11]	
$MgCl_2{\cdot}6H_2O$	pyridine	115 °C	Baum[11]	
$Mg(NO_3)_2{\cdot}6H_2O$	pyridine	115 °C	Baum[11]	
$Mg(OAc)_2{\cdot}4H_2O$	pyridine	115 °C	Baum[11]	
$Mg(ClO_4)_2$	acetone or MeOH, +pyridine	100 °C	Baum[12]	
$Mg(ClO_4)_2$	pyridine	115 °C	Fuhrhop[13]	TPP[33]
$MgCl_2$	DMF	153 °C	Adler[14]	TPP, TPC, A, C, D; B,[34] D[35]
Mg(acac)$_2$	quinoline	270 °C	Buchler[15]	D[36]
$Mg(OAc)_2{\cdot}4H_2O$	DMSO	189 °C	Strell[16]	
PhSMgI	CH_2Cl_2 + thiophene	25 °C	Isenring[17]	
BHT-MgI[c]	CH_2Cl_2 + diethyl ether	25 °C	Isenring[17]	TPP,[37] TPC,[38] E[39]
BHT-MgI + BHT-Li	thiophene	50−80 °C	Isenring[17]	
BHT-MgI + BHT-Li	thiophene	50 °C	Zass[18]	
BHT-MgI + Me_4pip-Li	ether + thiophene	25 °C	Wasielewski[19]	
MgO	H_2O	100 °C	Herrmann[20]	F
$Mg(OAc)_2{\cdot}4H_2O$[d]	3% MeOH/KOH + DMF	153 °C	Kadish[21]	TPP
$Mg(OAc)_2{\cdot}4H_2O$	H_2O, pH 5	80 °C	Szulbinski[22]	G
$MgCl_2{\cdot}6H_2O$	DMF	153 °C	Ong[23]	TPP

[a] Abbreviations: BHT, the anion of $2,6(t\text{-}Bu)_2\text{-}4\text{-}CH_3C_6H_2OH$; Me_4pip, the anion of 2,2,6,6-tetramethylpiperidine; TPP, *meso*-tetraphenylporphyrin; TPC, *meso*-tetraphenylchlorin; A, *meso*-tetrakis(4-chlorophenyl)porphyrin; B, *meso*-tetrakis(4-methoxyphenyl)porphyrin; C, *meso*-tetrakis(4-tolyl)porphyrin; D, *meso*-tetrakis(4-pyridyl)porphyrin; E, polymeric esters of *meso*-tetrakis(4-carboxyphenyl)porphyrin; F, TPP-tetrasulfonic acid; G, *meso*-tetrakis(4-(*N*-ethyldimethylamino)phenyl)porphyrin. Nonpreparative methods for magnesium insertion include monolayer assemblies,[24] metalation with magnesium dipyrromethene complexes,[25] or transmetalation of iron porphyrins with Grignard reagents.[26] [b] Presumed structure of reagent prepared in situ. [c] Many other solvents also were examined. [d] Literature states $Mg(OAc)_2$. [e] Temperature not given. [f] Other magnesium tetraarylporphyrins have been prepared by unspecified methods.[40]

No preparative syntheses have been developed for inserting magnesium into ortho-substituted tetraarylporphyrins.

As part of a program employing facially-encumbered porphyrin building blocks[41,42] in the synthesis of multiporphyrin light-harvesting arrays,[43] we had need of a mild method for preparing the magnesium chelates of *meso*-tetraarylporphyrins, particularly those bearing ortho-substituents and various peripheral functional groups. Such "facially-encumbered" porphyrins constitute a key element of highly soluble multiporphyrin arrays. We now report a simple and mild method for preparing magnesium chelates of *meso*-substituted porphyrins using commercially-available materials. We have investigated the dependence of the metalation yields on the nature of the solvent, base, and magnesium reagent, explored the concentration ratios of magnesium reagent and porphyrin, and applied this method to the synthesis of the magnesium chelates of several facially-encumbered porphyrins (Chart 1).

Experimental Section

Materials. CH_2Cl_2 (Fisher reagent grade) was distilled from K_2CO_3. $CHCl_3$ (99.8%, ACS spectrophotometric grade, stabilized with amylenes) was obtained from Aldrich. All mentions of $CHCl_3$ in this paper refer to $CHCl_3$ stabilized with amylenes unless noted otherwise. Toluene (ACS certified) was obtained from Fisher. THF was distilled from $LiAlH_4$. All other solvents were reagent grade and were used as received. Triethylamine was distilled from CaH_2 or used as received from Fluka (puriss). The other amines and all magnesium reagents were obtained from Aldrich. The $MgBr_2{\cdot}O(Et)_2$ was obtained as large clumps. These were pulverized with mortar and pestle, and the finely pulverized powder was used in all experiments. The magnesium reagents, which hydrate upon exposure to moist air, were weighed out on the open benchtop without special precautions but also without undue delays so as to minimize hydration. Chromatography was performed on alumina (Fisher A-540). The free base porphyrins used in the metalation studies were chlorin-free.

Analysis of Magnesium Insertion Reactions. The reaction optimization studies (Tables 2−4) were performed in 20 mL scintillation vials with vigorous magnetic stirring at room temperature. All reactions in CH_2Cl_2, $CHCl_3$, or toluene were heterogeneous, involving a slurry

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Chart 1. Structures of free base porphyrins

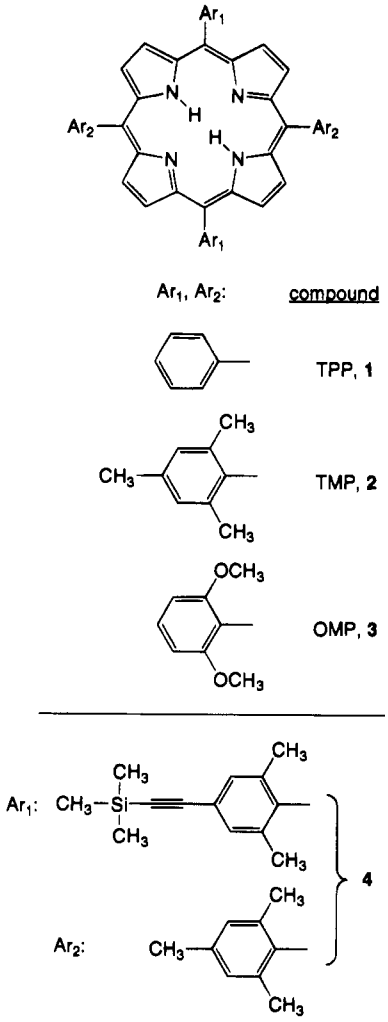

Table 2. Formation of MgTPP with Different Magnesium Reagents

		% yield of MgTPP					
		$MgCl_2$	$MgBr_2$		$MgBr_2$·O(Et)$_2$		MgI_2
time (min)	solvent	10 equiv[a]	10 equiv[a]	40 equiv[b]	10 equiv[a]	40 equiv[b]	10 equiv[a]
10	CH_2Cl_2	0	2	93	25	>95	56
30		0	2	>95	44	>95	>95
60		0	2	>95	54	>95	>95
10	$CHCl_3$	0	1	86	63	>95	>95
30		0	1	>95	90	>95	>95
60		0	2	>95	>95	>95	>95
10	toluene	0	0	12	3.8	>95	49
30		0	0	51	4.2	>95	87
60		0	0	88	4.7	>95	>95

[a] 2 mM TPP, 10 equiv of magnesium reagent, and 40 mM TEA at room temperature. [b] 2 mM TPP, 40 equiv of magnesium reagent, and 160 mM TEA at room temperature.

of the magnesium reagent in a solution of the porphyrin. The order of addition of materials was solvent and stir bar, magnesium reagent, amine, and then porphyrin as a concentrated solution in the same solvent. In a few cases (e.g., with concentrated porphyrin solutions) the magnesium reagent was added to a solution of the porphyrin and the amine. The order of addition is not significant except for the fact that, in the absence of a base, $MgBr_2$ or MgI_2 reagents and porphyrins form green mixtures. Samples (~100 μL) were removed from the reaction mixtures and diluted with toluene (3 mL). Absorption spectra were collected using a HP8452A spectrometer, and spectra were deconvoluted (HP89532Q) to determine the percent metalation. Yield determinations at the extremes of little reaction or near total reaction are sensitive to slight baseline shifts and other spectral artifacts;

Table 3. Solvent Effects on Formation of MgTPP[a]

	% yield of MgTPP	
solvent[b]	t = 30 min	t = 12 h
acetone	0	0
acetonitrile[c]	0	0
ethanolic $CHCl_3$[d]	53	>95
dichloromethane	>95	>95
diethyl ether	>95	>95
dimethyl sulfoxide	0	0
DMF	0	0
ethyl acetate	9	66
pyridine	0	0
THF	9	14

[a] Reactions were performed with 2 mM TPP, 40 equiv of $MgBr_2$·O(Et)$_2$, and 160 mM TEA at room temperature. [b] 50% this solvent, 50% CH_2Cl_2. The TPP was added as a 4 mM solution in CH_2Cl_2 to an equal volume of the solvent containing the $MgBr_2$·O(Et)$_2$ and TEA. In some solvents (diethyl ether, dimethyl sulfoxide, DMF) the $MgBr_2$·O(Et)$_2$ dissolved. [c] Much of the porphyrin precipitated, but that remaining in solution was not metalated. [d] $CHCl_3$ containing 0.75% ethanol.

Table 4. Role of Bases in Formation of MgTPP[a]

	$MgBr_2$·O(Et)$_2$	MgI_2	
base	30 min	5 min	30 min
DIEA[b]	64	>95	>95
tetramethylpiperidine[c]	>95	85	>95
triethylamine	64	90	>95
diethylamine	0	4	49
DBMP[d]	*g*	*g*	*g*
DBU[e]	2	3	5
DBN[f]	1	2	3

[a] Reactions were performed with 2 mM TPP, 10 equiv of magnesium reagent, and 40 mM base at room temperature in CH_2Cl_2. [b] *N,N*-Diisopropylethylamine. [c] 2,2,6,6-Tetramethylpiperidine. [d] 2,6-Di-*tert*-butyl-4-methylpyridine. [e] 1,8-Diazabicyclo[5.4.0]undec-7-ene. [f] 1,5-Diazabicyclo[4.3.0]non-5-ene. [g] A green mixture with some MgTPP present.

consequently, apparent yields of 95.5−100% have been stated as >95% and those of <1% have been reported as 0%. Absorption spectral parameters were taken from the literature for TPP and MgTPP[44] and were determined for TMP (ϵ_{514} = 23 900 M^{-1} cm^{-1}, ϵ_{420} = 406 000 M^{-1} cm^{-1} in toluene) and MgTMP (vide infra). The absence of residual free base porphyrin in the isolated magnesium porphyrins was confirmed by fluorescence excitation spectroscopy (λ_{em} 720 nm). ^1H NMR spectra were collected at 300 MHz. Axial ligands were identified by comparing spectra in $CDCl_3$ with and without addition of a small amount (2−4%) of CD_3OD. Yield calculations based on the mass of isolated magnesium porphyrin are not corrected for axial ligands or solvent of crystallization. Porphyrin mass spectra were determined by plasma desorption mass spectrometry.[45]

Magnesium Tetraphenylporphyrin (MgTPP). A sample of 100 mg (0.16 mmol) of chlorin-free TPP (**1**) was dissolved in 8 mL of CH_2Cl_2 in a one-neck round-bottom flask. Then 0.446 mL (3.2 mmol) of triethylamine was added followed by 413 mg (1.6 mmol) of $MgBr_2$·O(Et)$_2$. The mixture was stirred magnetically at room temperature. After 15 min the metalation appeared complete as judged by absorption spectroscopy. The mixture was diluted with 25 mL of CH_2Cl_2, washed with 5% $NaHCO_3$ (2 × 25 mL), dried (Na_2SO_4), and filtered, and the filtrate was concentrated to 4−5 mL. Chromatography on an alumina column (3 × 15 cm, poured in CH_2Cl_2 containing 0.1% triethylamine) with CH_2Cl_2 elution yielded residual TPP. Elution with CH_2Cl_2/acetone (1:1) afforded fractions that were concentrated, triturated with hexanes, and evaporated to dryness, affording 95 mg (93% yield): λ_{abs} (toluene) 426, 524, 564, 604 nm; λ_{em} 608, 663 nm; $C_{44}H_{28}N_4$-

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Mg calcd mass 636.2, obsd 636.2; ^{1}H NMR ($CDCl_3$) δ 8.85 (s, 8 H, β-pyrrole), 8.20 (m, 8 H, o-PhH), 7.72 (m, 12 H, m-, p-PhH).

Magnesium Tetramesitylporphyrin (MgTMP). A solution of 150 mg (0.19 mmol) of TMP (**2**)[46] in 15 mL of CH_2Cl_2 was treated with 0.662 mL (3.8 mmol) of *N,N*-diisopropylethylamine and 528 mg (1.9 mmol) of MgI_2 with stirring at room temperature. After 10 min the mixture was diluted with 50 mL of CH_2Cl_2, washed with 10% $NaHCO_3$ (2 × 50 mL), dried (Na_2SO_4), and filtered, and the filtrate was concentrated to 5 mL. Chromatography on alumina with $CHCl_3$ afforded the magnesium porphyrin contaminated with a trace of free base porphyrin (detectable only by fluorescence excitation spectroscopy). This mixture was rechromatographed on an alumina column (poured in toluene) with toluene/acetone (8:2), affording 138 mg (90% yield): λ_{abs} in toluene (log ϵ) 406 (4.68), 428 (5.65), 526 (4.47), 566 (4.3), 604 (3.9) nm; λ_{em} 605, 663 nm; $C_{56}H_{52}N_4Mg$ calcd mass 804.4, obsd 804.6; ^{1}H NMR ($CDCl_3$) δ 8.58 (s, 8 H, β-pyrrole), 7.26 (m, 8 H, m-ArH), 2.62 (s, 12 H, p-CH_3), 1.84 (s, 24 H, o-CH_3). This metalloporphyrin was also prepared in 95% yield by reaction of 150 mg (0.19 mmol) of TMP in 10 mL of toluene with 0.53 mL (3.8 mmol) of triethylamine and 0.491 g (1.9 mmol) of $MgBr_2{\cdot}O(Et)_2$ at 60 °C for 1 h, followed by chromatography on alumina with toluene/acetone (8:2).

Magnesium *meso*-Tetrakis(2,6-dimethoxyphenyl)porphyrin. A solution of 75 mg (0.088 mmol) of OMP (**3**)[47] in 25 mL of $CHCl_3$ (stabilized with amylenes) was treated with 0.245 mL (1.76 mmol) of triethylamine followed by 227 mg (0.88 mmol) of $MgBr_2{\cdot}O(Et)_2$. After being stirred magnetically at 65 °C overnight (10.5 h), the mixture was diluted with 75 mL of $CHCl_3$, washed with 5% $NaHCO_3$ (3 × 50 mL), dried (Na_2SO_4), and filtered, and the filtered residue was washed with $CHCl_3$ in order to dissolve the precipitated porphyrin. The $CHCl_3$ solutions were combined and concentrated, affording 45 mg (58% yield): λ_{abs} ($CHCl_3$) 428, 526, 566, 604 nm; λ_{em} 608, 663 nm; $C_{52}H_{44}N_4O_8Mg$ calcd mass 876.3, obsd 876.3; ^{1}H NMR (DMF-d_7) δ 8.59 (s, 8 H, β-pyrrole), 7.77 (m, 4 H, p-PhH), 7.15 (m, 8 H, m-PhH), 3.48 (s, 24 H, CH_3).

Magnesium 5,15-Dimesityl-10,20-bis(2,6-dimethyl-4-((trimethylsilyl)ethynyl)phenyl)porphyrin. A 5.3 mL toluene solution of 50 mg (0.053 mmol) of 5,15-dimesityl-10,20-bis(2,6-dimethyl-4-((trimethylsilyl)ethynyl)phenyl)porphyrin (**4**)[42] was treated with triethylamine (148 μL, 1.06 mmol) followed by $MgBr{\cdot}O(Et)_2$ (137 mg, 0.53 mmol). The mixture was stirred at 60 °C for 2 h, then diluted with 20 mL toluene, washed with 5% $NaHCO_3$ (3 × 25 mL), dried (Na_2SO_4), and filtered, and the filtrate was concentrated to 4−5 mL. Chromatography on alumina (2.5 × 15 cm) with toluene containing 0.1% triethylamine gave the free base porphyrin (7 mg, 14%), and enrichment with acetone (1−15%) eluted the magnesium porphyrin (41 mg, 80% yield): λ_{abs} (toluene) 428, 526, 566, 604 nm; λ_{em} 606, 663 nm; $C_{64}H_{64}N_4Si_2Mg$ calcd mass 968.4, obsd 968.4; ^{1}H NMR ($CDCl_3$) δ 8.63 (s, 4 H, β-pyrrole), 8.53 (s, 4 H, β-pyrrole), 7.60 (m, 4 H, m-ArH), 7.25 (m, 4 H, m-ArH), 2.60 (s, 6 H, p-CH_3), 1.84 (s, 24 H, o-CH_3), 0.36 (s, 18 H, CH_3Si).

Results

Reaction Conditions for Magnesium Insertion. We began a survey of reaction methods using TPP as a model compound. In order to develop a robust method with wide applicability, all studies were performed in standard glassware using reagent grade solvents under an air atmosphere. After a period of exploration, we found that TPP in toluene rapidly metalates at room temperature upon exposure to excess $MgBr_2$ and triethylamine (TEA). These studies were then expanded to include other magnesium halides, solvents, and bases. These experiments served to optimize the reaction conditions, establish the scope of application, and provide mechanistic insight into the reaction.

The time courses for magnesium insertion with four magnesium halide reagents in three noncoordinating solvents in the presence of TEA are shown in Table 2. The reactions were performed using 2 mM TPP at room temperature in well-stirred flasks. All of the reactions are heterogeneous. The effectiveness of the metalation reagent increases in the series $MgCl_2 \ll MgBr_2 < MgBr_2{\cdot}O(Et)_2 < MgI_2$, and CH_2Cl_2 and $CHCl_3$ (stabilized with amylenes) gave better results than toluene.

Three observations augment the data in Table 2. First, we noticed considerable variation in results with $MgBr_2$, and somewhat less so with $MgBr_2{\cdot}O(Et)_2$, on different occasions and with different batches of solvents for these dilute reactions (2 mM TPP, 10 equiv of magnesium reagent). For example, the yield of MgTPP varied from 2 to 74% after 30 min with $MgBr_2$ in CH_2Cl_2 and from 44 to >95% with $MgBr_2{\cdot}O(Et)_2$. Yields of 4, 16, 23, and 26% were obtained after 10 min with $MgBr_2{\cdot}O(Et)_2$ in four different batches of toluene. Yields at the low end of these ranges were typical, and these are reported in Table 2. However, in every case when parallel experiments were performed, metalation was several times faster with $MgBr_2{\cdot}O(Et)_2$ than with $MgBr_2$. Second, any magnesium incorporation tended to occur rapidly (within 10 min) with much slower subsequent change in metalloporphyrin yield. Third, with these dilute reaction mixtures the magnesium reagents tended to clump on the walls of the flask in spite of vigorous stirring. We attribute these results to inactivation of the magnesium reagents by hydration with water in the solvents (and perhaps by coating of the solid reagent surface with amine−hydrogen halide complexes), an effect that is pronounced under these dilute reaction conditions. Magnesium halides hydrate readily, and experiments with $MgBr_2{\cdot}6H_2O$ gave no magnesium porphyrin.

High yields can be achieved with dilute porphyrin solutions in reagent grade solvents by using a larger excess of magnesium reagent. When 40 equiv of $MgBr_2$ was employed, the magnesium chelate formed in quantitative yield and at a rate faster than that with 10 equiv of $MgBr_2{\cdot}O(Et)_2$ (Table 2). Similarly, 40 equiv of $MgBr_2{\cdot}O(Et)_2$ gave quantitative metalation in each solvent within 10 min. However, 40 equiv of $MgCl_2$ in refluxing $CHCl_3$ gave no MgTPP after 30 min and only yielded 30% after 14.5 h. In these studies the reaction mixtures contained free-flowing slurries of the magnesium reagents.

The requirement for excess magnesium reagent was investigated using a more concentrated solution of TPP (8 mM) and a TEA concentration 2 times that of the magnesium reagent. With various amounts of $MgBr_2{\cdot}O(Et)_2$ the yield of MgTPP after 10 min was 0% (1 equiv), 20% (3.16 equiv), and >95% (10 equiv). With various amounts of MgI_2 the yield of MgTPP after 10 min was 2% (1 equiv), >95% (3.16 equiv), and >95% (10 equiv). Thus excess magnesium reagent is necessary for metalation under these conditions.

The tolerance of the metalation reaction toward 10 solvents was examined using 40 equiv of $MgBr_2{\cdot}O(Et)_2$ and a corresponding amount of TEA (Table 3). Strongly coordinating solvents inhibit the reaction. Interestingly, $MgBr_2{\cdot}O(Et)_2$ dissolved in diethyl ether but upon addition of TEA a white precipitate formed. The metalation proceeded smoothly upon addition of TPP. The formation of a precipitate upon addition of TEA indicates specific interactions of the amine with the magnesium reagent.

The effects of seven bases were examined using $MgBr_2{\cdot}O(Et)_2$ or MgI_2 in CH_2Cl_2 (Table 4). The reaction with MgI_2 is rapid, and 5 min time points were required to identify distinctions among the most effective bases, diisopropylethylamine (DIEA), TEA, and 2,2,6,6-tetramethylpiperidine. Subtle interactions among bases and magnesium reagents were observed, as 2,2,6,6-

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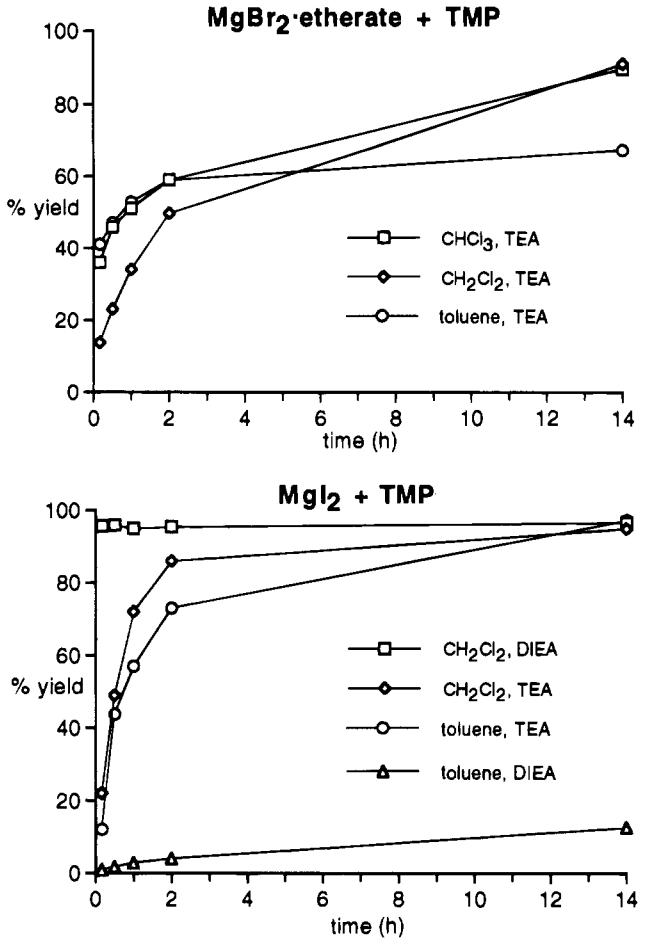

Figure 1. Formation of MgTMP at room temperature with 8 mM TMP, 10 equiv of magnesium reagent, and 160 mM base. The first three data points were collected at 10, 30, and 60 min. The TMP was not completely soluble in $CHCl_3$ but rapidly went into solution.

tetramethylpiperidine gave the best results with $MgBr_2{\cdot}O(Et)_2$ and DIEA gave the best results with MgI_2.

Applications. Tables 2–4 show that considerable latitude exists in the selection of solvent (CH_2Cl_2, $CHCl_3$, toluene), magnesium reagent ($MgBr_2$, $MgBr_2{\cdot}O(Et)_2$, MgI_2), and base (triethylamine, 2,2,6,6-tetramethylpiperidine, diisopropylethylamine) for magnesium insertion. In general, the best conditions that we have found employ a high concentration (>5 mM if possible) of the porphyrin, 10 equiv of magnesium reagent, and 20 equiv of base. Though it is possible to use less than 10 equiv of magnesium reagent in highly concentrated reactions, the best results are achieved when sufficient reagent is employed to remain free-flowing in the solvent. For reactions at <2 mM porphyrin concentration, a larger excess of magnesium reagent is beneficial. The reaction can be performed at ambient or higher temperatures. The selection of the solvent is made on the basis of the solubility of the porphyrin and the desired reaction temperature, since the boiling points of these solvents range from 39 °C (CH_2Cl_2) to 61 °C ($CHCl_3$) to 110 °C (toluene).

We investigated the insertion of magnesium into tetramesitylporphyrin (TMP, **2**) at room temperature using the conditions identified in the studies with TPP. TMP can be metalated at room temperature in over 50% yield in 2 h with six different combinations of reagents, solvents, and bases (Figure 1). The best conditions involve MgI_2 in CH_2Cl_2 with DIEA, which gives >95% yield of MgTMP within 10 min. Toluene is quite attractive as a solvent since the solubility of TMP increases in the series $CHCl_3$ < CH_2Cl_2 < toluene. The preparative-scale metalation of TMP was performed by using MgI_2 and DIEA in CH_2Cl_2 at room temperature for 10 min or with $MgBr_2{\cdot}O(Et)_2$ and TEA in toluene at 60 °C for 1 h. The trans-substituted porphyrin building block **4** was converted to the magnesium chelate in 80% yield by treatment for 2 h at 60 °C in toluene with 10 equiv of $MgBr_2{\cdot}O(Et)_2$.

In contrast to TMP, *meso*-tetrakis(2,6-dimethoxyphenyl)-porphyrin (OMP, **3**) gave no observable metalation with $MgBr_2{\cdot}O(Et)_2$ at room temperature in CH_2Cl_2. OMP has high solubility in CH_2Cl_2 or $CHCl_3$ but is relatively insoluble in toluene, the reverse of the solubility properties of TMP. Quantitative metalation was achieved with $MgBr_2{\cdot}O(Et)_2$ in refluxing $CHCl_3$.

When the room-temperature metalation conditions using $MgBr_2{\cdot}O(Et)_2$ and TEA or 2,2,6,6-tetramethylpiperidine were applied to tetraphenylchlorin (TPC), multiple products were formed. MgTPC could be isolated, but the yields were low. However, the metalation with MgI_2 and DIEA in CH_2Cl_2 at room temperature proceeded cleanly and MgTPC was the major product. A comprehensive investigation of magnesium insertion into synthetic and naturally-occurring hydroporphyrins will be published subsequently.

One of our goals is to prepare multiporphyrin arrays comprised of porphyrins in diverse metalation states.[43] We performed an experiment to determine whether magnesium insertion could be accomplished in the presence of zinc porphyrins without exchange. Exposure of ZnTPP (2 mM) to excess metalating reagent (40 equiv of $MgBr_2{\cdot}O(Et)_2$ and 160 mM TEA in CH_2Cl_2 at room temperature) for 17 h showed no detectable MgTPP by TLC analysis. Upon addition of a sample of TPP, MgTPP formed rapidly, indicating the integrity of the reaction conditions. Thus ZnTPP does not undergo metal exchange under prolonged exposure to the conditions for forming MgTPP. Though ZnTPP is not particularly susceptible to trans metalation,[48] these experiments confirm the gentle nature of the magnesium insertion conditions.

Purification and Characterization. The magnesium porphyrins are easily isolated from the reaction mixtures by a basic aqueous wash to remove magnesium salts, followed by short-column chromatography to remove any free base porphyrin. Chromatography of the magnesium porphyrins must be done with care. Exposure of a solution of MgTPP in CH_2Cl_2 to silica gel resulted in 25% demetalation in 1 h. Though no demetalation was observed upon prolonged exposure to silica gel in CH_2Cl_2 containing 0.1% triethylamine, for safe measure we chromatographed the magnesium porphyrins on alumina rather than silica.

Magnesium porphyrins avidly bind one or two axial ligands. Indeed, all X-ray structures of magnesium tetraarylporphyrins have pentacoordinate or hexacoordinate magnesium.[23,34,49,50] Axial ligands such as water or methanol can hydrogen-bond to solvent molecules, causing their incorporation into the crystal lattice, as seen in the structures of $MgTPP(H_2O)(2\text{-picoline})_2$,[23] $MgTPP(H_2O)(acetone)_2$,[50] and $MgTPP(CH_3OH)_2(acetone)_2$.[50] The axial ligands yield peaks in the upfield region of ^1H NMR spectra of magnesium porphyrins in solution. For example, one sample of MgTPP in $CDCl_3$ showed resonances consistent with exchanging diethyl ether (1.5 molecules per porphyrin), and one spectrum ($CDCl_3$) of MgTMP purified by chromatography with CH_2Cl_2 and acetone showed the presence of 2.5 CH_2Cl_2 and 2

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acetone molecules per porphyrin. The spectrum of MgOMP was obtained in DMF-d_7, which displaces bound axial ligands. The plasma desorption mass spectra of the magnesium porphyrins showed strong parent ions lacking axial ligands, indicating the integrity of the metalloporphyrin.

Discussion

The insertion of magnesium into porphyrins, as shown in eq 1, is a conceptually rather simple reaction. In practice, the

$$H_2\text{-porphyrin} + MgX_2 \rightarrow Mg\text{-porphyrin} + 2HX \quad (1)$$

successful implementation of this reaction requires careful selection both of the magnesium reagent and of the reaction conditions. The reaction conditions must provide compatibility with the metal insertion process and at the same time not provide pathways for formation of unreactive magnesium complexes. Our results show that magnesium insertion occurs smoothly in a noncoordinating (and nonionizing) solvent with a nonnucleophilic base and the magnesium reagent $MgBr_2$, $MgBr_2{\cdot}O(Et)_2$, or MgI_2. A quantitative thermodynamic and kinetic analysis of this process that treats the lability of the magnesium ligands, the nature and concentration of various magnesium species in solution, the mechanism of metal insertion including changes in the coordination sphere of magnesium, and the role of the amine including its contributions to the driving force by binding liberated acid, is not yet possible. The following discussion provides a qualitative analysis of key aspects of the reaction conditions leading to magnesium insertion.

Magnesium has a strong propensity to form octahedral complexes. Magnesium is too large (ionic radius 0.72 Å)[51] to fit snugly in the core of the porphyrin and instead generally rests out-of-plane with square-pyramidal coordination.[52] Magnesium porphyrins are relatively stable kinetically in nonacidic solvents but under acidic conditions are rapidly demetalated with rate proportional to the coordinating strength of the medium.[53] Thus magnesium porphyrins do not represent the most stable coordination complexes for magnesium. Magnesium forms octahedral complexes with a variety of ligands, including H_2O, alcohols, pyridine, and some other nitrogenous bases, though magnesium has much higher affinity for oxygen than for nitrogen ligands.[54] Relevant examples of octahedral complexes include $MgBr_2(pyridine)_6$,[55] $MgBr_2(CH_3OH)_6$,[56] $MgBr_2(THF)_4$,[57] $MgBr_2(THF)_4(H_2O)_2$,[58] and $MgI_2(CH_3OH)_6$.[59] $MgBr_2$ also forms the progression of etherates $MgBr_2{\cdot}nEt_2O$ in solution where $n = 1-3$,[60,61] and both $MgBr_2$ and MgI_2 self-associate in diethyl ether solution.[62] A similar series with tetrahydrofuran is observed yielding $MgBr_2(THF)_n$ where $n = 2-4$.[58,63] Weak association complexes as are formed with diethyl ether do not significantly inhibit the reaction, unlike complexes with more strongly coordinating ethers such as tetrahydrofuran. The hydration complex $MgBr_2(H_2O)_6$ is unreactive toward metalation, as is $MgBr_2{\cdot}O(Et)_2$ in pyridine. We attribute the difficulty of magnesium insertion in coordinating solvents to the formation of hexacoordinate magnesium complexes that are more stable than the magnesium porphyrin.

In a noncoordinating slightly basic medium, magnesium insertion occurs smoothly with $MgBr_2$, $MgBr_2{\cdot}O(Et)_2$, or MgI_2. $MgBr_2$ and MgI_2 show the octahedral CdI_2 (or brucite) structure[64] while the crystal structure of the dietherate $MgBr_2{\cdot}2Et_2O$ shows independent molecules with a tetracoordinated magnesium at the center of a distorted tetrahedron.[61] To our knowledge the X-ray structure of $MgBr_2{\cdot}O(Et)_2$ has not been determined. The hydration of each of these magnesium reagents is an exothermic process.[65] The magnesium halides MgX_2 form complexes with amines, and these also are readily hydrolyzed, forming the more stable hydrated complexes.[66] Thus the crystal lattice of each of these reagents only provides partial stabilization compared with the ideal octahedral complex. One interpretation is that these reagents have energy comparable to or higher than that of the magnesium porphyrin, and that in the absence of a coordinating solvent the insertion of magnesium into the porphyrin ligand represents a pathway for forming a more stable coordination complex. The energy of these reagents could be less than that of the magnesium porphyrin if the complexation of the liberated acid by the amine is a significant driving force in the overall reaction. This simple thermodynamic analysis lacks quantitation but it does account in a straightforward way for the observations of no metalation in coordinating solvents and facile metalation in noncoordinating solvents.

The different metalation results obtained with $MgCl_2$, $MgBr_2$, and MgI_2 are striking. The lattice energies of the magnesium halides, $MgCl_2$ (595 kcal/mol), $MgBr_2$ (571 kcal/mol), and MgI_2 (545 kcal/mol),[67] mirror the trend observed in metalation efficiency, with the most efficient reagent having the least lattice stabilization. For magnesium insertion it is not necessary to form separated magnesium and halide ions, as measured by the lattice energies, only to solubilize a sufficient amount of an appropriate magnesium species so that reaction can occur on a reasonable time scale. The greater solubility expected in the series $MgCl_2 < MgBr_2 < MgI_2$, which parallels the lattice energies, may also contribute to the observed differences in metalation. The energy gained by formation of the hydrogen halides (HCl, 103 kcal/mol; HBr, 87 kcal/mol; HI, 71 kcal/mol bond energy) is significant (though offset by breaking two porphyrinic N–H bonds); however these trends in bond strengths are opposite the observed differences in metalation. The overall driving force contributed by amine complexation of the hydrogen halide is not known but is not expected to be the source of the differences observed with the different magnesium halides.

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The amine functions to neutralize the hydrogen halide liberated during magnesium insertion and perhaps to assist in the deprotonation of the free base porphyrin. In addition to these functions as a Bronsted base, amines can form weak complexes with $MgBr_2$ and MgI_2.[66] Some differences in reaction rates observed with amine−magnesium−solvent combinations in metalations of TPP and TMP may be due to amine−magnesium interactions. In the absence of a base, the reaction mixture turned green, indicating the presence of the protonated porphyrin, and little or no metalation was observed.

In summary, magnesium insertion occurs with a reagent that is not in a stable octahedral form, that has labile ligands, and that can be partially solubilized in a slightly basic medium that does not yield a stable octahedral magnesium complex. It is ironic that in one of the earliest accounts of magnesium insertion (Table 1), Fischer *et al.* chose nearly the ideal reagent ($MgBr_2$) but used pyridine as the solvent, requiring reflux to achieve metalation.[3] A prevalent approach for metal insertion is to use a metal halide in the solvent DMF at reflux. These conditions are designed to provide high solubility for both the metal halide and the porphyrin.[14] Our approach is fundamentally distinct from that with DMF−$MgCl_2$. Achieving mutual solubility of both reactants is important, but not at the expense of forming inactive coordination complexes of magnesium. Given magnesium's preference for octahedral coordination and the greater stability of many magnesium complexes with strong donor ligands compared with the magnesium porphyrin, starting with $MgBr_2$, $MgBr_2{\cdot}O(Et)_2$, or MgI_2 in a noncoordinating milieu provides the opportunity to insert magnesium into porphyrins under the mildest conditions.

Outlook

Magnesium can be inserted into tetraarylporphyrins with readily available reagents under rather mild conditions. This general strategy for metal insertion may also be applicable to other metalloporphyrins that currently can only be prepared under forcing conditions. In addition to gaining access to a wide variety of synthetic magnesium porphyrins, this method may be applicable to the formation of magnesium chelates of nonporphyrinic ligands. The ability to form magnesium porphyrins quite easily may prove useful in separation schemes, given the pronounced affinity of the magnesium chelates for polar chromatographic media. A mixture that is difficult to separate can be subjected to the conditions for magnesium insertion, and the magnesium chelate(s) can be separated by chromatography and then demetalated under gentle acidic conditions. Finally, the field of artificial photosynthesis has relied almost exclusively on the more readily available zinc porphyrins. Magnesium porphyrins have a 4−5-fold greater fluorescence quantum yield ($\Phi_f = 0.15$),[33,68] commensurably longer singlet excited-state lifetime ($\tau = 9$ ns),[33,68] and 100−200 mV lower oxidation potential[13,69] compared with zinc porphyrins. The method reported here should make magnesium porphyrins available for a variety of biomimetic studies.

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