

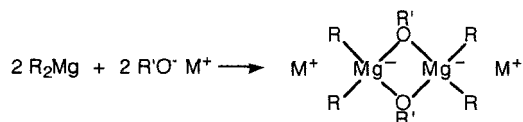
Reactions of Grignard Reagents with an Azacrown Ether; Formation of RMg(14N4)^+ and XMg(14N4)^+ Cations and $\text{R}_n\text{MgX}_{3-n}^-$ and X^- Anions¹

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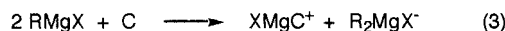
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Organomagnesates that are true anions can be prepared from diorganomagnesium compounds (R_2Mg). Addition, for example, of some macrocyclic compounds leads to $\text{RMg}(\text{macrocycle})^+$ cations and organomagnesate anions such as R_3Mg^- ,^{3–5} and addition of sodium or potassium alkoxides leads to alkoxy substituted organomagnesate anions.⁶ The behavior in reactions of these organomagnesates differs from that of R_2Mg compounds or Grignard reagents.^{3,7,8}

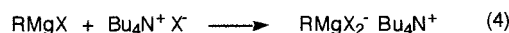


The goal of this work was to prepare organomagnesate anions directly from Grignard reagents (RMgX) rather than from R_2Mg . This would avoid preparation of R_2Mg , which usually includes a tedious and sometimes low yield precipitation of a MgX_2 complex from an RMgX solution,^{9,10} and make more efficient use of R groups; note the use in the reactions above of four R groups to make one organomagnesate ion.¹¹ One approach is to add a coordinating agent (C) to RMgX to form $\text{RMgC}^+ \text{RMgX}_2^-$

(eq 1). In initial experiments, addition of some macrocyclic compounds to diethyl ether or THF solutions of Grignard reagents led to precipitation of $\text{MgX}_2(\text{macrocycle})$. Materials of composition $\text{RMgX}(\text{THF})_n$ ($n = 1-2$) could be prepared, however, and addition of 14N4 (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) to benzene solutions of these usually did not result in precipitation. A preliminary study¹² found that some of these solutions had RMgC^+ and RMgX_2^- (eq 1) but others had anion X^- (eq 2) or cation XMg(C)^+ (eq 3). This paper

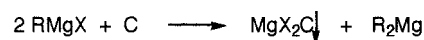


describes a more extensive study of such reactions to delineate the influence of structure and reactant ratio on the outcome. Reactions of RMgX with a halide salt (eq 4), another potential conversion of RMgX to an organomagnesate ion, also are described.



Results and Discussion

RMgX and Macrocycles in Ether Solvents. Addition of 15C5 (15-crown-5), 14N4, or 2,1,1-cryptand to an Et_2O or THF solution of RMgX (R is one of several primary R groups and X is Cl, Br, or I) led to immediate formation of a precipitate. The ¹H NMR spectra of the



solutions remaining from reactions of EtMgBr or NpMgCl (Np is neopentyl) with 15C5 (1:1) in Et_2O showed little 15C5 but strong absorptions characteristic of Et_2Mg or Np_2Mg . The solution remaining after adding 15C5 to a THF solution of 3-MeBuMgBr (3-MeBu is 3-methylbutyl) had a greatly increased R/Br ratio. The precipitates, very insoluble in benzene, therefore are $\text{MgX}_2(15\text{C5})$, the crown ether (C) behaving as does dioxane⁹ to precipitate MgX_2 and leave R_2Mg in solution. In fact, the precipitate that formed upon adding 15C5 to an Et_2O solution of *i*-BuMgBr (1:2) lacked isobutyl groups since a solid-state ¹³C NMR spectrum had only a single absorption (δ 66.6).¹³ The single absorption for the 15C5 carbons suggests a structure in which Mg is coordinated equally to all oxygen atoms of the crown ether rather than to fewer oxygens.

Preparation of $\text{RMgX}(\text{THF})_n$. A more successful approach used Grignard reagents prepared in THF and then heated at reduced pressure (60–95 °C, 0.01–0.001 Torr).¹⁴ Table 1 lists the R/X and THF/R ratios of typical solids or oils that resulted. Because of side reactions¹⁰ during their formation, Grignard reagents tend to have

(1) Portions of this work are taken from ref 2 and Chubb, J. E. Ph.D. Thesis, The Pennsylvania State University, 1997.

(2) Pajerski, A. D. Ph.D. Thesis, The Pennsylvania State University, 1990.

(3) Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432.

(4) Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510.

(5) Pajerski, A. D.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2660.

(6) For example, see: Hanawalt, E. M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4983.

(7) Georgoulis, C.; Gross, B.; Ziegler, J.-C. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1971**, *273*, 378.

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(10) Reviews and references for many aspects of organomagnesium chemistry: Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 4. Lindsell, W. E. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 1, Chapter 3. *Handbook of Grignard Reagents*; Silverman, G. S., Rakita, P. E., Eds.; Marcel Dekker: New York, 1996. Wakefield, B. J. *Organomagnesium Methods in Organic Synthesis*; Academic: London, 1995.

(11) After reaction of R_3Mg^- with a substrate, two R groups may still be in an organomagnesate species (e.g., perhaps $\text{R}_2\text{MgOCR}'_2\text{R}^-$ after addition to $\text{R}'_2\text{C}=\text{O}$) but will have a different reactivity than the first R to react.

(12) Fabicon, R. M.; Pajerski, A. D.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 9333.

(13) Additional absorptions should have been seen if the solid had isobutyl groups; the solid-state ¹³C NMR spectrum² of *i*-BuMg(15C5)⁺ fluorenone²⁻ has the expected isobutyl absorptions.

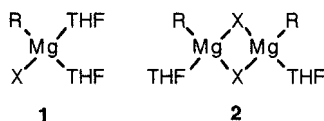
(14) A related procedure has been described¹⁵ in which benzene or toluene is added to a Grignard reagent prepared in THF. The solvent is evaporated, and benzene or toluene addition and solvent removal are repeated.

Table 1. RMgX(THF)_n Preparations and Their Reactions with 14N4

RMgX	R/X ^a	THF/R ^b	14N4/Mg ^c	δ		XMg ⁺ /RMg ⁺ ^f	δ	
				RMg(14N4) ⁺ ^d	XMg(14N4) ⁺ ^e		RMg ⁺ ^g	RMg ⁻ ^h
MeMgI	0.98	2.0	0.5 (insol) 1.0 (insol)					
EtMgI		1.0	0.5 1.0 (ppt)	3.77 4.12			-0.73 -0.73	0.17
<i>i</i> -BuMgI	0.96	1.25	0.5 1.0 (ppt)	3.38 4.39			-0.78 -0.78	0.18
<i>i</i> -PrMgI	0.96	1.0	0.5 1.0 (insol)	3.30			-0.54	0.32
<i>p</i> -CH ₃ C ₆ H ₄ MgI	0.97	1.0	0.5 1.0 (insol)	3.22			7.37	8.47
EtMgBr		1.0	0.5 1.0 (insol)	3.84			-0.71	0.18
<i>i</i> -BuMgBr		1.0	0.5 1.0 (ppt)	3.90 4.59			-0.78 -0.70	0.33
Me ₃ CCH ₂ MgBr	1.01	1.01	0.51 (ppt) 1.05 (ppt)	3.94 4.40			-0.55 -0.51	0.17, 0.41
3-MeBuMgBr	1.05	0.79	0.54 1.04	4.10 4.60			-0.80 -0.79	0.10
2-EtBuMgBr	0.98	1.0	0.5 1.0 (ppt)	3.54 4.45			-0.86 -0.81	0.17
<i>i</i> -PrMgBr	0.91	1.62	0.51 1.06 (ppt)	3.85 4.50	4.22 4.85	0.18 0.14	-0.55 -0.55	0.27
<i>s</i> -BuMgBr	1.04	1.14	0.50 1.02 (ppt)	3.65 4.38	3.88 4.60	? ⁱ 0.06	-0.74 -0.74	0.30 0.30
Me ₂ C=CHMgBr	0.94	1.2	1.0 (insol)					
<i>p</i> - <i>t</i> -BuC ₆ H ₄ MgBr	0.94	1.2	0.5 1.0 (insol)	3.50			7.31	8.39
<i>p</i> -MeOC ₆ H ₄ MgBr	0.96	1.0	0.5 1.0 (insol)	<i>j</i>			7.20	8.12
<i>i</i> -BuMgCl	0.98	1.0	0.5	ca. 3.9	4.00	0.22	-0.80	0.22
Me ₃ CCH ₂ MgCl	0.92	1.7	1.50	3.90	4.16	1.05	-0.50	0.25, 0.37
<i>i</i> -PrMgCl	0.96	0.74	0.50 1.14	3.92 3.91	4.21 4.20	0.64 0.62	-0.54 -0.52	0.27 0.20
<i>s</i> -BuMgCl	0.97	1.01	0.54 1.02	3.75 3.85	3.95 4.08	? ⁱ 1.40	-0.70 -0.75	0.33 0.30

^a Ratio of R to X in RMgX(THF)_n determined by titration. ^b Ratio of THF to R in RMgX(THF)_n determined by ¹H NMR spectroscopy. ^c Ratio of added 14N4 to R of RMgX(THF)_n. "Insol" indicates that solubility was too low to permit routine ¹H NMR spectroscopy. "Ppt" indicates that a precipitate formed but solubility was sufficient for an NMR spectrum. ^d Most downfield ¹H NMR absorption of 14N4 of RMg(14N4)⁺. ^e Most downfield ¹H NMR absorption of 14N4 of XMg(14N4)⁺. ^f Ratio of XMg(14N4)⁺ to RMg(14N4)⁺ determined by ¹H NMR spectroscopy. ^g ¹H NMR absorption of α -H or o -H of R of RMg(14N4)⁺. ^h ¹H NMR absorption of α -H or o -H of R of RMgX₂⁻, R₂Mg, etc. ⁱ Overlap with a THF absorption precluded determination of this ratio using the most downfield 14N4 absorption of each cation. NMe absorptions could not be used because of overlap with *s*-Bu absorptions. ^j This absorption was inadvertently not recorded; the spectrum was later destroyed in the earthquake in Kobe, Japan.

R/X ratios less than 1. To provide compositions closer to R₁Mg₁X₁, some preparations used a lower temperature or a THF–benzene solvent. The R/X ratio of RMgX(THF)_n solids or oils, however, did not depend greatly on the temperature, pressure, or time used for removing the solvent. The THF/R ratios fall in the range of 1–2, usually near either 1 or 2 but dependent on the conditions of solvent removal. Removal of most of the THF from an *i*-BuMgBr, *i*-BuMgI, or 2-EtBuMgBr (2-EtBu is 2-ethylbutyl) preparation, for example, leaves a white solid, having a THF/R ratio of 2.0 and very soluble in benzene; heating one of these solids at ~90 °C under vacuum for 12 h leaves a liquid, having a THF/R ratio of ~1.0 and also very soluble in benzene. By contrast, MeMgI retains two THFs even after lengthy heating at ~100 °C (10⁻³ Torr). The species probably have structures such as **1** and **2**.¹⁰



When the RMgX(THF)_n materials that remain after solvent removal are liquids (which generally are viscous),

solids gradually separate from them over a period of weeks. Analysis indicates that the solids (which are insoluble in benzene) obtained from *i*-BuMgI, 2-EtBuMgBr, and *i*-PrMgI contain MgX₂ and that the remaining liquids have high R/X ratios. All of a solid dissolves when a mixture of the solid and supernatant liquid is heated in benzene to about 60 °C.

Most RMgX(THF)_n preparations are very soluble in benzene at ambient temperature. For example, the 2-EtBuMgBr preparation described in Table 1 is a liquid miscible in all portions with benzene. Even the solid MeMgI (mp 84–86 °C) and EtMgI (mp 154–165 °C) preparations are soluble to the extent of ~1.5 M. The *p*-TolMgBr preparation was least soluble, but the *p*-*tert*-butylphenylmagnesium bromide (mp 70–80 °C) and *p*-methoxyphenylmagnesium bromide (a gummy solid) preparations form approximately 0.3 and 1.0 M solutions, respectively.

This procedure is a convenient preparation of Grignard reagents that are soluble in a hydrocarbon. Grignard reagents have been prepared directly in hydrocarbon solvents before,^{10,16} but such reactions often are difficult

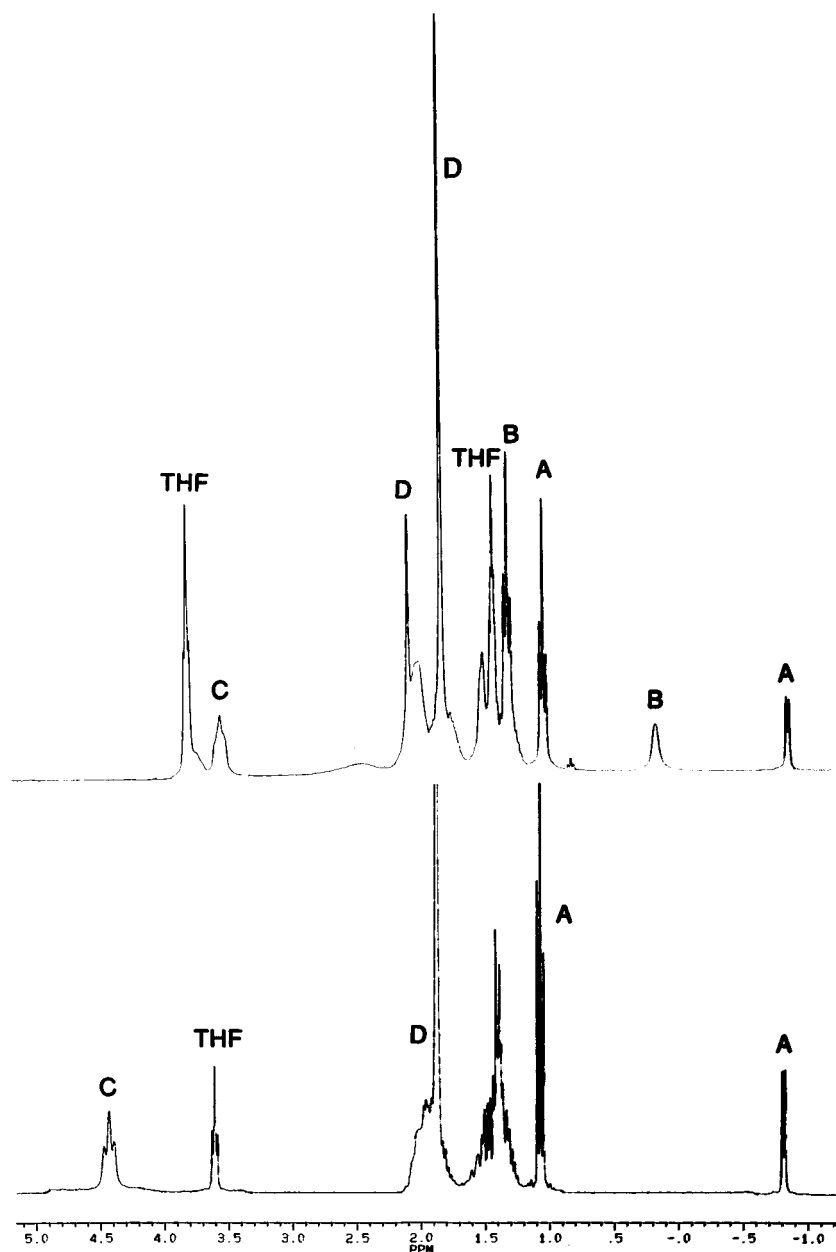


Figure 1. ^1H NMR spectra of benzene- d_6 solutions prepared from $\text{RMgBr}(\text{THF})$ (R is 2-ethylbutyl) and 14N4. The upper spectrum, of $\text{RMg}(\text{14N4})^+ \text{RMgBr}_2^-$ (~ 0.15 M), resulted from adding 0.5 equiv of 14N4 to an $\text{RMgBr}(\text{THF})$ solution. The lower spectrum, of $\text{RMg}(\text{14N4})^+ \text{Br}^-$ (~ 0.15 M), resulted from adding 1 equiv of 14N4 to an $\text{RMgBr}(\text{THF})$ solution. R absorptions of $\text{RMg}(\text{14N4})^+$ are labeled A, and those of RMgBr_2^- are labeled B. The $(\text{NCHHCH}_2\text{CHHN})$ absorption of $\text{RMg}(\text{14N4})^+$ discussed in the text is labeled C; some other 14N4 absorptions of this cation are labeled D. THF has absorptions at $\delta \sim 1.3\text{--}1.4$ and $\sim 3.6\text{--}3.7$.

to initiate and produce solutions having high R/X ratios. Grignard reagents also have been prepared in hydrocarbons containing one or a few equivalents of an additive such as diethyl ether or triethylamine.^{10,17} Such solutions prepared^{15,18} in benzene containing a small amount of THF may resemble those reported here.

Reactions of $\text{RMgX}(\text{THF})_n$ and 14N4. Preparations that resulted from combining these reactants in benzene generally were stable for weeks. The products depended on the 14N4/ RMgX ratio and the nature of R and X.

$\text{RMg}(\text{14N4})^+ \text{RMgX}_2^-$. The reaction of 2-EtBuMgBr and 14N4 (2:1) is an example of this pathway. The ^1H NMR spectrum (Figure 1, upper spectrum) has two sets of R and one set of 14N4 absorptions. Absorption intensities indicate one of the Rs and the 14N4 to be 1:1. Absorptions of this R and the 14N4 are similar to those found for $\text{RMg}(\text{14N4})^+$ in the presence of other anions.^{2,19,20} The CH_2Mg absorption ($\delta -0.86$) is considerably upfield from that of R_2Mg or $\text{RMgX}(\text{THF})$, and the 14N4 absorptions are more complex than those of free 14N4. The second set of R absorptions, equal in intensity to the first, is assigned to RMgX_2^- . These absorptions (of

(16) For example, see: Smith, W. N., Jr. *J. Organomet. Chem.* **1974**, 64, 25 and references therein. Wakefield, B. J. *Organomet. Chem. Rev.* **1966**, 1, 131 and references therein.

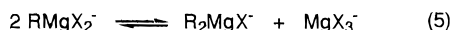
(17) A recent study: Tuulmets, A.; Mikk, M.; Panov, D. *J. Organomet. Chem.* **1996**, 523, 133.

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(19) Tang, H.; Richey, H. G., Jr. *Organometallics* **1996**, 15, 4891.

(20) Tang, H.; Parvez, M.; Richey, H. G., Jr. *Organometallics* **1996**, 15, 5281.

CH_2Mg at δ 0.17, for example) are sometimes broader than the R absorptions of $\text{RMg}(\text{14N4})^+$. The broadness may be due to equilibration that is not fast on the NMR time scale of species, those in eq 5 for example, having



the average composition RMgX_2^- . The two noncation absorptions for the neopentyl species may be due to equilibration that is sufficiently slow to permit observation of absorptions of discrete species.²¹ The word "anion" below means whatever equilibrating species are responsible for the set of R absorptions observed in addition to that of $\text{RMg}(\text{14N4})^+$.

$\text{RMg}(\text{14N4})^+ \text{X}^-$. The reaction of 2-EtBuMgBr and 14N4 (1:1) is an example of this pathway. X^- formation is indicated by the ^1H NMR absorptions (Figure 1, lower spectrum) of $\text{RMg}(\text{14N4})^+$ but no absorptions for an anion. $\text{RMg}(\text{14N4})^+ \text{X}^-$ formation is frequent when the 14N4/ $\text{RMgX}(\text{THF})_n$ ratio is 1 and the amount of 14N4 is therefore sufficient to convert all $\text{RMgX}(\text{THF})_n$ to $\text{RMg}(\text{14N4})^+$. $\text{RMg}(\text{14N4})^+ \text{X}^-$ generally is less soluble than $\text{RMg}(\text{14N4})^+ \text{RMgX}_2^-$; 14N4/ RMgX ratios of 0.5 usually lead to solutions but ratios of 1 often lead to precipitates (solubility $< \sim 0.1$ M). When some of a precipitate from a solution prepared with a 14N4/ RMgX ratio of 1 did dissolve in benzene- d_6 , the ^1H NMR spectrum indicated the presence principally or only of $\text{RMg}(\text{14N4})^+ \text{X}^-$ (and THF). The spectrum of a solution of the precipitate from an *i*-BuMgBr and 14N4 (1:1) reaction after recrystallization from benzene had no THF absorptions.

The position of just one $\text{RMg}(\text{14N4})^+$ absorption, the most downfield 14N4 absorption, is very dependent on the anion. That absorption, due to four hydrogens, wanders considerably. In Figure 1, for example, this absorption of $\text{RMg}(\text{14N4})^+ \text{RMgX}_2^-$ is at δ 3.54, and that of $\text{RMg}(\text{14N4})^+ \text{X}^-$ is at δ 4.45. Crystal structures of $\text{PhMg}(\text{14N4})^+ \text{Ph}_3\text{Mg}(\text{THF})^-$,² $\text{MeMg}(\text{14N4})^+ \text{Cp}^-$,² and $\text{MeMg}(\text{14N4})^+ \text{Me}_3\text{Cd}^-$ ²⁰ show Ph or Me and the four N-Me groups to lie above one face of 14N4 and four H's ($\text{NCHHCH}_2\text{CHHN}$) to lie above the other face. It must be because these H's jut into the solution at the location providing the least hindered approach to the center of positive charge that their absorptions are uniquely influenced by the anion.

$\text{XMg}(\text{14N4})^+ \text{R}_2\text{MgX}^-$. Besides $\text{RMg}(\text{14N4})^+$ absorptions, some solutions had a second set of 14N4 absorptions but no corresponding R absorption. The second NCH_3 (δ 2.01 ± 0.06) and $\text{NCHHCH}_2\text{CHHN}$ absorptions were downfield from the $\text{RMg}(\text{14N4})^+$ absorptions (NCH_3 at δ 1.80 ± 0.05), as expected for a macrocycle encapsulating XMg^+ rather than RMg^+ . Crown ether absorptions of $\text{RAIX}(\text{crown})^+$, for example, are downfield from those of $\text{R}_2\text{Al}(\text{crown})^+$.²²

$\text{XMg}^+/\text{RMg}^+$ ratios are indicated in Table 1. If $\text{XMg}(\text{14N4})^+$ were the only cation, then the anion composition would be R_2MgX^- . R absorptions of the anion should be relatively larger when some $\text{XMg}(\text{14N4})^+$ is present than when $\text{RMg}(\text{14N4})^+$ is the only cation (compare eqs 1 and 3). The ratio of the absorptions of R of $\text{RMg}(\text{14N4})^+$ and of the "anion" corresponding to an observed $\text{XMg}(\text{14N4})^+ /$

$\text{RMg}(\text{14N4})^+$ ratio can be calculated.²³ The observed and calculated ratios are in reasonable accord, confirming the formation of some $\text{XMg}(\text{14N4})^+$.

Other NMR Observations. Sharp absorptions for any 14N4 not incorporated into $\text{RMg}(\text{14N4})^+$ or $\text{X}(\text{14N4})^+$ indicated that any exchange of this 14N4 with that in the cations was slow relative to the NMR time scale. The absorption positions of excess 14N4 and also of the THF present are similar but often not identical to those of solutions in which each is the only component. Probably, there is some bonding of a heteroatom of THF or excess 14N4 to the magnesium of an anion.

Effects of Reactant Ratio, X, and R on Product Composition. When the 14N4/ $\text{RMgX}(\text{THF})_n$ ratio is 0.5, the cation is either $\text{RMg}(\text{14N4})^+$ or a mixture of that cation and $\text{XMg}(\text{14N4})^+$. The anion composition is RMgX_2^- when only $\text{RMg}(\text{14N4})^+$ is observed, but the R/X ratio is greater when some $\text{XMg}(\text{14N4})^+$ is present. When the 14N4/ $\text{RMgX}(\text{THF})_n$ ratio is 1 and X is I or Br, preparations often have substantial precipitates. Where solubility permits obtaining ^1H NMR spectra, $\text{RMg}(\text{14N4})^+ \text{X}^-$ is the principal or only species; the solids have this composition and probably also are composed of $\text{RMg}(\text{14N4})^+$ and X^- ions. Because of its smaller anion, it is reasonable that $\text{RMg}(\text{14N4})^+ \text{X}^-$ is less soluble than $\text{RMg}(\text{14N4})^+ \text{RMgX}_2^-$. A study of 14N4 and *i*-BuMgBr(THF) at ratios ranging from 0 to 1 (some precipitate noted at ratios ≥ 0.7) found all 14N4 to be incorporated into *i*-BuMg-(14N4)⁺ and, except for the $\text{NCHHCH}_2\text{CHHN}$ absorption, positions of absorptions of this cation to be virtually constant. As the 14N4/*i*-BuMgX(THF) ratio increased, the positions of the other set of R absorptions changed from those of *i*-BuMgBr(THF) to those attributed to *i*-BuMgX₂⁻, diminished in intensity, and vanished at a ratio of 1.

Reactions of RMgCl , in contrast to those of RMgI and RMgBr , do not produce significant amounts of X^- . 14N4/ RMgCl ratios of 0.5 and of 1 lead to essentially identical ^1H NMR spectra except for absorptions of free 14N4 when the ratio is 1. The similar intensities of the R absorptions of $\text{RMg}(\text{14N4})^+$ and the anion rule out formation of substantial amounts of Cl^- .

$\text{X}(\text{14N4})^+$, not observed when X is I, is seen for some R's when X is Br and always when X is Cl. With the same R group, $\text{CIMg}(\text{14N4})^+$ is formed to a greater extent than $\text{BrMg}(\text{14N4})^+$. As expected since their formation involves the same reactant stoichiometry (eqs 1 and 3), the $\text{XMg}(\text{14N4})^+/\text{RMg}(\text{14N4})^+$ ratio is insensitive to the 14N4/ RMgX ratio. Equation 6 makes it evident that the



$\text{XMg}(\text{14N4})^+/\text{RMg}(\text{14N4})^+$ ratio is affected by the relative stabilities of X and of R in both a cation and an "anion". Less $\text{RMg}(\text{14N4})^+$ when R is secondary rather than primary may be due to a steric effect. A large R group probably is relatively less favorable in $\text{RMg}(\text{14N4})^+$ than in the anion, proximity of R to the N-methyl groups of 14N4 being a critical factor.²⁴ Decreasing $\text{XMg}(\text{14N4})^+$ in the series $\text{Cl} > \text{Br} > \text{I}$ also may be due to size.

(21) Since they usually have unequal intensities, the two absorptions for CH_2Mg are not due to the H's being diastereotopic.

(22) Richey, H. G., Jr.; Bergstresser, G. L. *Organometallics* **1988**, *7*, 1459.

(23) For a system described completely by eqs 1 and 3 and having $\text{R/X} = 1$, $(\text{R in anions})/(\text{R in } \text{RMg}(\text{14N4})^+) = (2 - Z)/Z$ where $Z = [\text{RMg}(\text{14N4})^+]/([\text{RMg}(\text{14N4})^+] + [\text{XMg}(\text{14N4})^+])$. This formula can be elaborated to include R/X ratios other than 1, but this refinement is not warranted because of limitations to the accuracy of integrating absorptions and small alterations in the R/X ratio introduced by minor amounts of precipitation and by effects of reaction with traces of water and oxygen.

(24) See also the results and discussion in ref 19.

Reactions of RMgX(THF)_n with Other Coordinating Agents. 15N5 (1,4,7,10,13-pentamethyl-1,4,7,10,13-pentaazacyclopentadecane) was less prone than 14N4 to coordinate with RMg^+ . Addition of 15N5 to a solution of 3-MeBuMg(14N4)⁺ 3-MeBuMgBr₂[−] led to no significant changes in the ¹H NMR spectrum except appearance of 15N5 absorptions. When 15N5 was added to a (3-MeBu)₂Mg solution followed by addition of 14N4, the only cation absorptions were of 3-MeBuMg(14N4)⁺.

Addition of 15C5 to benzene solutions of several RMgX(THF) preparations resulted in large precipitates whose nature depended on the R and X. With EtMgBr(THF) and 15C5 (2:1), for example, the ¹H NMR spectrum of the remaining solution had absorptions only of THF and some 15C5. With *i*-BuMgBr(THF) and 15C5 (1:1), the remaining solution had absorptions of *i*-Bu₂Mg (altered somewhat in position by coordination to 15C5 and THF oxygens); the ~2:1 ratio of *i*-Bu and 15C5 absorptions indicated that the precipitate must be $\text{MgBr}_2(15\text{C}5)$. Heat and reduced pressure were used to remove solvent from the precipitate that formed from 15C5 and *i*-BuMgI(THF). Most ¹H NMR absorptions of the solution formed from completely dissolving a portion of this precipitate in benzene-*d*₆ are those expected^{2,5} for *i*-BuMg(15C5)⁺. The CH₂Mg absorption (δ −0.38) is typical for $\text{RCH}_2\text{Mg(15C}5)^+$ cations, and the 15C5 absorption is two equal multiplets (δ 3.32 and 3.78), indicating that the faces of the crown ether ring are different. The solution must contain *i*-BuMg(15C5)⁺ I[−], and the solid probably also has these ions.

Upfield absorptions (δ ca. −0.4) for some CH₂Mg groups in solutions formed by addition to 2-EtBuMgBr(THF) of 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane, an acyclic counterpart of 14N4, or 2,5,8-trimethyl-2,5,8-triazanonane probably are due to forming some RMgC^+ cations. Because of the success in using 14N4, these coordinating agents were not investigated further.

Reactions of RMgX(THF)_n with $\text{Bu}_4\text{N}^+ \text{Br}^-$. Addition of a halide salt to an RMgX (eq 4) solution is a potential synthesis of RMgX_2^- ; in fact, addition of a tetraalkylammonium halide to $\text{RMgX}^{25,26}$ or $\text{R}_2\text{Mg}^{8,26}$ does affect reactivity. We found that addition of 1 equiv of $\text{Bu}_4\text{N}^+ \text{Br}^-$ (itself soluble in benzene) to a benzene-*d*₆ solution (0.1–0.2 M) of a PrMgBr(THF) , *s*-BuMgBr(THF), *s*-BuMgCl(THF), or NpMgBr(THF) preparation led to separation of a second liquid phase.²⁷ ¹H NMR spectra show that the smaller, lower phase has much, and in some instances virtually all, of the solute. The presence of two phases would not necessarily impede preparative uses but would complicate mechanistic studies, and we did not pursue this approach.

Experimental Section

Procedures involving organometallic compounds were performed under an atmosphere of nitrogen (purified by passage

(25) Chastrette, M.; Amouroux, R. *Bull. Soc. Chim. Fr.* **1970**, 4348.

(26) Chastrette, M.; Amouroux, R.; Subit, M. *J. Organomet. Chem.* **1974**, 78, 303.

(27) Such phase separation is often noted when organometallic ions are formed in aromatic solvents. For a review, see: Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic: London, 1984; Vol. 1, Chapter 9.

(28) Fabicon, R. M.; Parvez, M.; Richey, H. G., Jr. *Organometallics* **1999**, 18, 5163.

(29) Day, R. A., Jr.; Underwood, A. L. *Quantitative Analysis*, 6th ed.; Prentice Hall: Englewood Cliffs, NJ, 1991; Chapter 22.

through columns of manganese oxide oxygen scavenger and 4 Å molecular sieves) using Schlenk techniques, a glovebox, and a vacuum line. Glassware was dried in an oven at 200 °C. ¹H NMR spectra were taken in benzene-*d*₆; absorptions are reported relative to internal benzene (C₆D₅H), taken as δ 7.15 ppm. Solid-state ¹³C NMR absorptions are reported (downfield) from the CH₃ absorption of external hexamethylbenzene, taken as δ 17.36. Immediately prior to use, diethyl ether and THF were distilled from sodium/benzophenone and dioxane was distilled from CaH₂. Benzene-*d*₆ (Aldrich or Cambridge Isotopes Laboratories) was stored over molecular sieves. Organic halides (Aldrich) were distilled from CaH₂ and stored over molecular sieves. Magnesium (usually Aldrich, 99.95%), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Aldrich or Strem), and 15-crown-5, (Aldrich) were used as received. 1,4,7,10,13-Pentamethyl-1,4,7,10,13-pentaazacyclopentadecane was prepared as described.²⁸ 2,5,8-Trimethyl-2,5,8-triazanonane (Aldrich) was distilled under vacuum, and it and 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane (Aldrich) were stored over molecular sieves. Tetrabutylammonium bromide was heated at reduced pressure (100 °C, 0.01 Torr) for 4 h.

Preparation of Grignard Reagents. Diethyl ether solutions were prepared in a conventional fashion. In a typical preparation of a THF solution, 1,2-dibromoethane (~100 mg) was added to a stirred mixture of Mg (1.46 g, 0.06 mol) and THF (40 mL) until signs of reaction were visible. A THF solution of the alkyl halide (0.05 mol) was added dropwise and heat was applied to maintain refluxing. Stirring and heating then were continued for several additional hours. Modified procedures were used for arylmagnesium bromides (preparation at 0 °C), TolMgI and *i*-PrMgI (a benzene–THF (1:1, v:v) mixed solvent), and *i*-BuMgI and *t*-BuMgBr (both 0 °C and the mixed solvent). The mixture then was centrifuged; THF was removed from the stirred supernatant liquid by gradually heating to 60–95 °C and reducing the pressure to 0.01–0.001 Torr. To titrate the residue for total base, a sample was hydrolyzed, and a phenolphthalein indicator solution added. Portions of a standard HNO₃ solution (0.10 M) were added until the solution was colorless and all solids had dissolved, and the solution was titrated to the phenolphthalein endpoint with a standard NaOH solution (0.10 M). This solution then was titrated for halide (Mohr method).²⁹ It was acidified with a few drops of HNO₃ solution to just remove the pink phenolphthalein color, and 1–2 drops of a K₂CrO₄ solution (5%) were added followed by titration with a standard AgNO₃ solution (0.10 M) to a change from yellow to brick red. In some instances, an aliquot of the THF solution of Grignard reagent also was titrated; the base/halide ratios were similar to those of the materials remaining after heating at reduced pressure. THF/R ratios of the residues were obtained from ¹H NMR spectra (benzene-*d*₆) by comparing intensities of the CHO absorption of THF and an absorption of R.

Preparation of Samples from RMgX(THF)_n and an Additive. An additive and a benzene-*d*₆ solution of an RMgX(THF)_n preparation were weighed into a vial equipped with a magnetic stirring bar. Concentrations were 0.1–0.5 M, those at the lower end of this range used when higher concentrations led to precipitates. Usually 0.5 mL of solution was prepared, but a larger scale was used when a second liquid phase formed and an NMR spectrum of the smaller phase was to be taken. The sample was stirred until it became homogeneous or no further dissolving took place and then was transferred to an NMR tube that had been modified by adding an extension of routine glass tubing to facilitate sealing with a flame. The tube was closed with a septum, removed from the glovebox, frozen in liquid nitrogen, and sealed at the extension. If precipitate was evident in the NMR tube, the tube was centrifuged to collect the precipitate at the unobserved (by the spectrometer) end.

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