Reactions of Diorganomagnesium Compounds and Cryptands or 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane: Formation of RMg(macrocycle)+ Cations and Organomagnesate Anions

Anthony D. Pajerski,[†] Diana M. Kushlan,[†] Masood Parvez,*[‡] and Herman G. Richey, Jr.*[†]

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, and Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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Many reactions of diorganomagnesium compounds (R_2Mg) and a cryptand or 14N4 (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) in benzene form solutions of RMg(macrocycle)+ and organomagnesate ions. With 14N4 or 2,1,1-cryptand and 2 equiv of R_2Mg, conversion to RMg-(macrocycle)+ and R_3Mg^- is complete. Conversion to RMg(macrocycle)+ tends to be less complete with 2,2,1-cryptand and with some R_2Mg compounds does not occur at all with 2,2,2-cryptand. Conversion to RMg(macrocycle)+ tends to be greater when R is *p*-tolyl rather than alkyl and the solvent is benzene rather than THF. A crystal structure of PhMg(14N4)+Ph$_3$Mg(THF)$^-$ is reported.

This paper describes an investigation of reactions of R_2Mg compounds with cryptands or 14N4 (14N4 = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane). A few reactions of R_2Mg compounds and cryptands have been reported to form RMg(cryptand)+ and organomagnesate ions. X-ray analysis of a solid obtained from Et$_2$Mg and 221C (221C = 2,2,1-cryptand) showed it to consist of EtMg(221C)+ ions (magnesium bonded to five of the seven heteroatoms of the cryptand) and Et$_6$Mg$_2^-$ ions (**1**, R = Et).[1] X-ray analysis found a solid that formed from
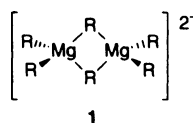
Np$_2$Mg (Np = neopentyl = Me$_3$CCH$_2$) and 211C (211C = 2,1,1-cryptand) to consist of NpMg(211C)+ ions (magnesium bonded to all heteroatoms of the cryptand) and Np$_3$Mg$^-$ ions.[1] NMR observations indicated that these ions persisted when the solid was dissolved[1] in benzene and also that a solution of TolMg(221C)+ and Tol$_3$Mg$^-$ (Tol = *p*-methylphenyl) resulted[2] from combining Tol$_2$Mg and 221C in benzene.[3] RMg(macrocycle)+ cations also formed from other reactants.[4] Grignard reagents RMgX(THF) and 14N4 in benzene formed RMg-(14N4)+, XMg(14N4)+, RMgX$_2^-$, and X$^-$, the composition depending on X, R, and the reactant ratio,[5] and some reactions

of R_2Mg, a cryptand or 14N4, and R_2Zn^6 or R_2Cd^7 formed solutions of RMg(macrocycle)+ and R_3Zn^- or R_3Cd^-. Some reactions of R_2Mg and 15-crown-5 or 18-crown-6 also form RMg(macrocycle)+ ions,[2,8] but the composition of accompanying anions is never as simple as R_3Mg^-, and R_2Mg(macrocycle) species having rotaxane structures[2,8,9] also are products.

Results

Only one X-ray crystal structure was obtained. Characterizations instead were based on NMR spectra of solutions. Benzene was most often the solvent. Solubility of the products from R_2-Mg−macrocycle reactions in benzene often was greater than in solvents (diethyl ether, THF) ordinarily used in organomagnesium chemistry, and the deuterated version of benzene needed for ^{1}H NMR studies is considerably less expensive than are deuterated ethers.

14N4 and Diorganomagnesium Compounds in Benzene. Preparations with (2-EtBu)$_2$Mg (2-EtBu = 2-ethylbutyl) in benzene are a good starting point since, unlike most other preparations, they are homogeneous. ^{1}H NMR spectra of solutions prepared in benzene-d_6 with a 2-EtBu$_2$Mg/14N4 ratio of 2 indicate essentially quantitative formation of 2-EtBuMg-(14N4)+ and 2-EtBu$_3$Mg$^-$.[3] A spectrum (Figure 1) shows two sets of 2-ethylbutyl absorptions. The smaller set of 2-ethylbutyl absorptions and the 14N4 absorptions are characteristic[10] of RMg(14N4)+ ions: for example, a CH$_2$Mg absorption is at

* To whom correspondence should be addressed. E-mail: parvez@ucalgary.ca; hgr@chem.psu.edu.
† The Pennsylvania State University.
‡ University of Calgary.
(1) Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432.
(2) Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510.
(3) Besides the absorptions attributed to RMg(macrocycle)+, NMR spectra showed only one other set of R absorptions (other than weak absorptions often seen for RH). This set could be due to R_3Mg^-, but could instead be due to a dimeric species (**1**) such as observed in one crystal structure if a process (such as cleavage to R_3Mg^- and recombination) that exchanges the structurally different R groups of **1** is rapid relative to the NMR time scale.
(4) Me$_2$Mg and 1,4,7-trimethyl-1,4,7-triazacyclononane in benzene produced a solid shown by X-ray analysis to contain "triple-decker" Me$_3$Mg$_2$-(macrocycle)$_2^+$ cations and Me$_8$Mg$_3^{2-}$ anions: Viebrock, H.; Behrens, U.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1257.

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(10) Reproductions of ^{1}H NMR spectra of RMg(14N4)+ where R is methyl,[11] ethyl,[7] 2-ethylbutyl,[5] isobutyl [Fabicon, R. M.; Pajerski, A. D.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 9333], or phenyl[12] are available.
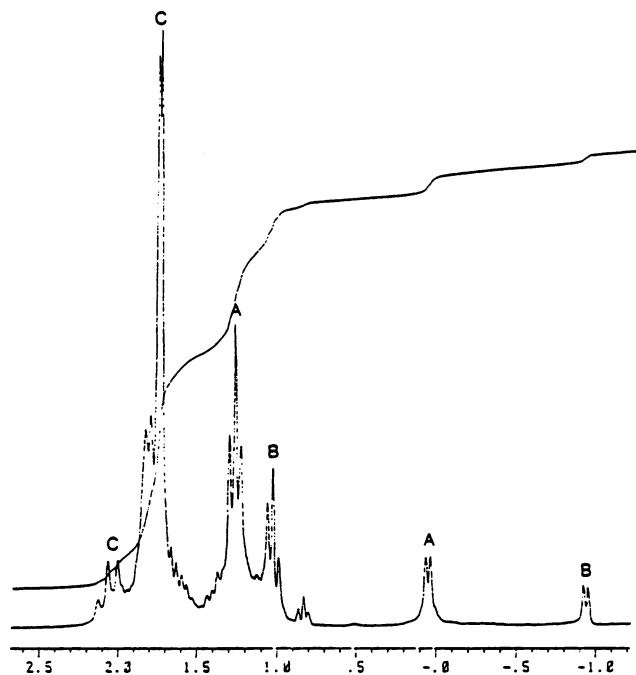
Figure 1. ^{1}H NMR spectrum (360 MHz) of a solution resulting from combining 2-EtBu$_2$Mg and 14N4 in benzene-d_6. Some absorptions of the alkyl group and macrocycle of 2-EtBuMg(14N4)$^+$ are labeled B and C, respectively. The ratio of reactants used to prepare this solution was ca. 2.2, so the "other" alkyl absorptions, labeled A, are somewhat larger than would correspond to the stoichiometry 2-EtBuMg(14N4)$^+$2-EtBu$_3$Mg$^-$, an example of how in such solutions all R groups that are not incorporated into a RMg-(macrocycle)$^+$ cation equilibrate rapidly.

much higher field (δ −0.91 in Figure 1) than that of 2-EtBu$_2$-Mg, and the 14N4 absorptions are more complex than those of uncoordinated 14N4. Except for a low-field absorption (δ 2.35 in Figure 1) for 4 H's of the 14N4, the positions of the RMg-(14N4)$^+$ absorptions are nearly the same with different accompanying anions.

Similar 2/1 preparations of other primary reagents (Et$_2$Mg, *i*-Bu$_2$Mg, Np$_2$Mg) and 14N4 led to formation of two liquid phases.[13] The lower phases, generally smaller and more viscous, contained most of the solute. ^{1}H NMR spectra of the lower phases (exemplified by the spectrum of an isobutyl preparation in Figure 2) had the features observed with the homogeneous 2-ethylbutyl system, indicating essentially quantitative formation of RMg(14N4)$^+$ and R$_3$Mg$^-$ ions.[3] Organometallic ions in aromatic solvents sometimes reside in such phases.[14]

Typical results for preparations with other Np$_2$Mg/14N4 reactant ratios are summarized in Table 1. With Np/14N4 ratios > 4, the positions of the ^{1}H NMR absorptions of NpMg(14N4)$^+$ were essentially constant, but the larger set of neopentyl absorptions increased in size relative to the NpMg(14N4)$^+$ set, shifted somewhat in position, and broadened. For most R$_2$Mg−macrocycle preparations, any RMg species other than RMg-(macrocycle)$^+$ affords only a single set of NMR absorptions (we will sometimes refer to this set as the "other" R absorptions), not surprising since R groups of species such as R$_3$Mg$^-$ and
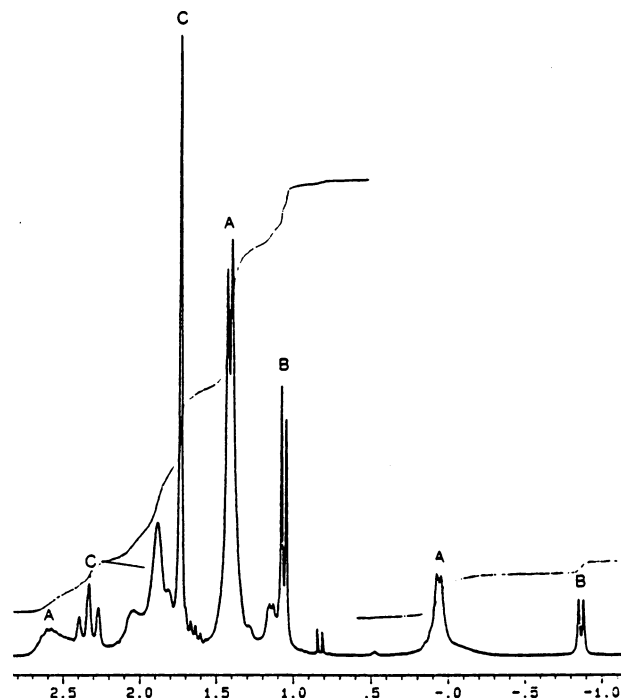
(11) Pajerski, A. D.; Squiller, E. P.; Parvez, M.; Whittle, R. R.; Richey, H. G., Jr. *Organometallics* **2005**, *24*, 809.

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(13) Me$_2$Mg−14N4 preparations furnished materials too insoluble to afford NMR spectra.

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Figure 2. ^{1}H NMR spectrum (200 MHz) of the lower phase resulting from combining *i*-Bu$_2$Mg Mg and 14N4 (2/1) in benzene-d_6. Absorptions of *i*-Bu$_3$Mg$^-$ are labeled A. Some absorptions of the isobutyl group and macrocycle of *i*-BuMg(14N4)$^+$ are labeled B and C, respectively.

R$_2$Mg are expected ordinarily to exchange rapidly relative to the NMR time scale. For preparations with Np/14N4 ratios < 4, cation absorptions also were essentially constant, and the ratio of the CH$_2$Mg absorption of the cation to that assigned to Np$_3$Mg$^-$ remained ca. 1/3; however, a second CH$_2$Mg and a second NCH$_3$ absorption were seen that had the same positions for different Np/14N4 ratios. We assign these absorptions to Np$_2$Mg(14N4) (eq 1), whose neopentyl groups must not exchange rapidly with those of Np$_3$Mg$^-$. The magnitudes of

$$\text{Np}_2\text{Mg} + 14\text{N4}$$

$$\text{Np}_2\text{Mg}(14\text{N4}) \qquad \text{NpMg}(14\text{N4})^+ + \text{Np}_3\text{Mg}^- \qquad (1)$$
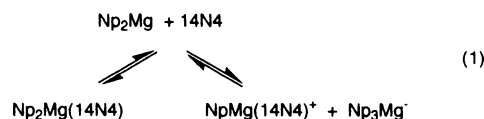
the equilibrium constants must be such that when Np/14N4 is ≤2, most neopentyl groups are in Np$_2$Mg(14N4); as Np/14N4 increases, an increasing portion are in NpMg(14N4)$^+$Np$_3$Mg$^-$, and at a Np/14N4 ratio of 4, most neopentyl groups are in these ions. At Np/14N4 ratios > 4, the absorptions of the "other" neopentyl groups increase and shift somewhat in position. Similar observations of ^{1}H NMR absorptions assigned to R$_2$-Mg(14N4) when R/14N4 was <4 were made with preparations in which R was 2-ethylbutyl.

(Methallyl)$_2$Mg (methallyl = CH$_2$=CMe-CH$_2$$^-$) and 14N4 in benzene led to a sticky oil. Homogeneous solutions resulted, however, by dissolving (methallyl)$_2$Mg in benzene containing 2 equiv of THF and then adding 0.5 equiv of 14N4. [1]H NMR spectra had two sets of methallyl absorptions in 3/1 ratio and 14N4 absorptions characteristic of RMg(14N4)$^+$ ions. The two sets of methallyl absorptions were dramatically different. The larger set, which we assign to (methallyl)$_3$Mg$^-$, had an absorption (δ 2.15) for the CH$_3$ group and one absorption (δ 2.82) for the two CH$_2$ groups. The CH$_2$ groups of methallyl organomagnesium compounds usually exhibit a common absorption;[15] even if the magnesium is associated with one of the allylic carbons,

Table 1. ^{1}H NMR Data for Np$_2$Mg$-$14N4 Preparations in Benzene-d_6^{a}

Np/14N4[b]	number of phases	anionic NpMg/Np(14N4)$^+$	NpMg(14N4)$^+$	Np$_2$Mg(14N4)	anionic NpMg	NCH$_3$ absorptions[d] δ	δ
∞	1				0.26 (100)		
4.7	2	3.5	−0.59 (22)		0.22 (78)	1.79	
4.0	2	3.0	−0.60 (25)		0.20 (75)	1.78	
2.3	1	ca. 3[e]	−0.58 (22)	0.11 (20)	0.22 (58)	1.79	2.07
1.3	1	ca. 3[e]	−0.58 (16)	0.10 (42)	0.23 (42)	1.79	2.09
0.8	1	ca. 3[e]	−0.59 (13)	0.07 (53)	0.20 (33)	1.76	2.08
0.5	1	ca. 3[e]	−0.59 (9)	0.06 (68)	0.20 (23)	1.76	2.09
0.3	1	f	−0.59 (ca. 2)	0.11 (ca. 98)	f	1.76	2.11

Columns 4–6 fall under the spanning header: **CH$_2$Mg absorptions δ (% of total CH$_2$Mg absorptions)[c]**

[a] In preparations having two phases, the data are for the denser phase. The concentration of 14N4 (in all forms) was ca. 0.2−0.4 M in homogeneous solutions, but much higher in the denser phases that separated from some preparations. [b] Determined from the ratio of all CH$_2$Mg absorptions to the CH$_3$ absorption of 14N4. [c] The percent composition was determined from areas of the various CH$_2$Mg absorptions. [d] The absorption at δ 1.76−1.79 was ca. 6 times greater than that at δ ca. −0.59. [e] The absorptions at δ ca. 0.20 and δ ca. 0.10 were broad and overlapping so that the measurements of relative areas for these peaks are only approximate. [f] The absorption at δ 0.11 was sufficiently broad and large to obscure any weak absorption that may have been present at δ ca. 0.20.

exchange of these carbons is rapid relative to the NMR time scale. The smaller set of absorptions, which we assign to (methallyl)Mg(14N4)$^+$, in addition to an absorption (δ 1.76) for the CH$_3$ group, had discrete absorptions for CH$_2$Mg (δ 0.66) and for $=$CH$_2$ (δ 4.19 and 4.22).[16] The CH$_2$ groups retain their identities and even the $=$C*H*H and $=$CH*H* hydrogens retain stereochemical integrity. That the CH$_2$ groups do not exchange rapidly is reasonable for (methallyl)Mg(14N4)$^+$ since steric interactions will make it difficult for both to simultaneously be near the magnesium.

One vinyl and two arylmagnesium compounds were investigated. (Me$_2$C$=$CH)$_2$Mg and 14N4 in 2/1 ratio formed a homogeneous solution in benzene. Absorptions for $=$CH at δ 5.43 and 6.30 (δ 5.96 in the reactant) indicated the presence of two vinyl groups in 1/3 ratio. The spectrum also had absorptions characteristic of 14N4 incorporated into RMg(14N4)$^+$.[17] With Tol$_2$Mg and 14N4 in 2/1 ratio, little material dissolved in benzene. A significant amount dissolved when lower ratios (e.g., 1/1) were used, and the solutions exhibited two sets of aryl absorptions in 1/3 ratio, the smaller set and the 14N4 absorptions characteristic[5,18] of TolMg(14N4)$^+$. Excess 14N4 promotes solubility but does not reduce the conversion of Tol$_2$Mg to ions as it did with Np$_2$Mg and 2-EtBu$_2$Mg. Preparations in benzene of Xyl$_2$Mg (Xyl = 3,5-dimethylphenyl), itself insoluble in that solvent, and 14N4 led to viscous, insoluble oils. Xyl$_2$Mg dissolved in benzene, however, when 2 equiv of THF was added. After addition to such a solution of 0.5 equiv of 14N4, the ^{1}H NMR spectrum (Figure 3) had two sets of xylyl absorptions in 1/3 ratio, the smaller set and the 14N4 absorptions having positions expected for XylMg(14N4)$^+$.

Crystal Structure of PhMg(14N4)$^+$Ph$_3$Mg(THF)$^-$. Only one effort to obtain crystals suitable for X-ray analysis was successful. Crystals that formed at the interface when pentane was layered over a THF solution prepared from Ph$_2$Mg and 14N4 consisted of PhMg(14N4)$^+$ and Ph$_3$Mg(THF)$^-$ ions (ORTEP drawing in Figure 4). Selected bond distances and bond
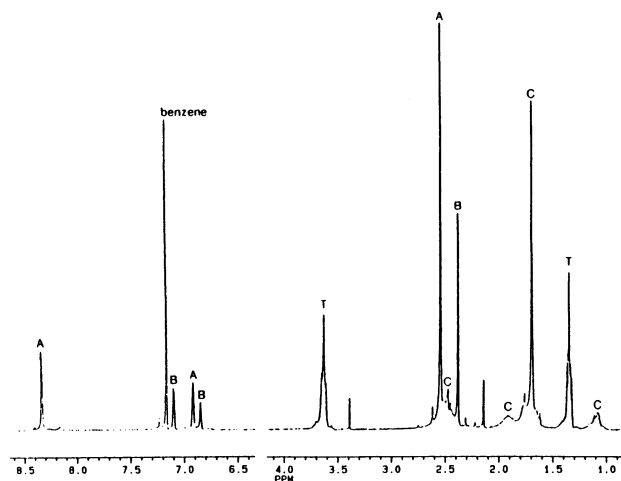
(15) Hutchinson, D. A.; Beck, K. R.; Benkeser, R. A.; Grutzner, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 7075, and references therein. Benn, R.; Lehmkuhl, H.; Mehler, K.; Rufinska, A. *J. Organomet. Chem.* **1985**, *293*, 1. Lehmkuhl, H.; Mehler, K.; Benn, R.; Rufinska, A.; Krüger, C. *Chem. Ber.* **1986**, *119*, 1054.

(16) The absorptions of the methallyl group of the cation are very similar to those reported for a benzene solution (no added THF) of (methallyl)-Mg(14N4)$^+$ In$^-$ (InH = indene),[11] although, in that case, only a single absorption was seen for $=$CH$_2$.

(17) The lowest-field multiplet of 14N4 is particularly far downfield (δ 3.85).

(18) Also compare with a PhMg(14N4)$^+$ spectrum.[12]

Figure 3. ^{1}H NMR spectrum (300 MHz) of a benzene-d_6 solution of Xyl$_2$Mg(14N4)$^+$Xyl$_3$Mg$^-$. Absorptions of the anion are labeled A. Absorptions of the aryl group and 14N4 of the cation are labeled B and C, respectively. An absorption of THF is labeled T (2 equiv of THF had been added to make the system soluble). The benzene absorption is due to C$_6$D$_5$H.

angles are listed in Table 2. The magnesium of the cation is bonded to the four 14N4 nitrogen atoms (0.719(2) Å above their mean plane) and to an apical phenyl group. The essentially identical Mg−N distances (average 2.24 Å) are similar to those in MeMg(14N4)$^+$Cp$^-$ and MeMg(14N4)$^+$Me$_3$Cd$^-$.[11,12] Even though bonds to sp^2 carbons ordinarily are shorter than to sp^3 carbons, the C−Mg distance (2.18 Å) is longer than in the MeMg(14N4)$^+$ structures (2.14 and 2.15 Å), probably a result of steric crowding with the phenyl group. The anion incorporates a THF, unlike the anion[1] in Np(211C)$^+$Np$_3$Mg$^-$ that also was recrystallized from THF. The manner in which the magnesium of the cation is enveloped makes it clear why specific interactions with donor molecules in solution are minimal. The structure of the cation also suggests why an accompanying anion in solution, which probably is frequently over the face of RMg-(14N4)$^+$ opposite from R and close to magnesium, would often be near the four NC*H*CH$_2$C*H*HN hydrogens, whose ^{1}H NMR absorption is sensitive to the anion.[19]

Cryptands and (Hexyl)$_2$Mg in Benzene. Preparations using (Hex)$_2$Mg (Hex = hexyl) are a convenient starting point since they were limited neither by low solubility nor separation of a

(19) In this connection, see views of the cation in a depiction of the unit cell in the Supporting Information.

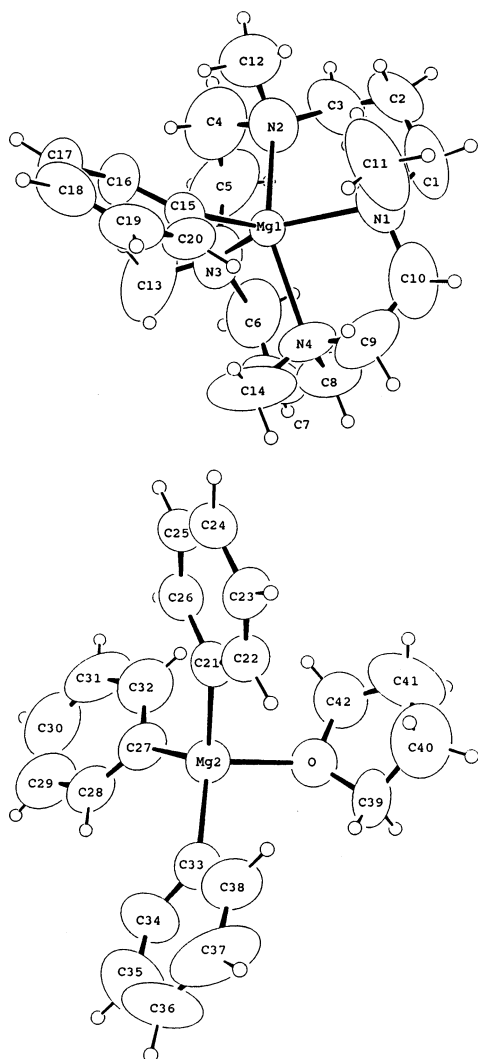**Figure 4.** ORTEP drawings of PhMg(14N4)$^+$ and Ph$_3$Mg(THF)$^-$. Atoms are shown with 50% probability ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Crystal Structure of PhMg(14N4)$^+$Ph$_3$Mg(THF)$^-$

		Bond Distances		
Mg(1)−N(1)	2.238(8)		Mg(2)−O	2.136(7)
Mg(1)−N(2)	2.223(8)		Mg(2)−C(21)	2.171(7)
Mg(1)−N(3)	2.233(7)		Mg(2)−C(27)	2.185(8)
Mg(1)−N(4)	2.246(7)		Mg(2)−C(33)	2.173(8)
Mg(1)−C(15)	2.183(8)			

|		Bond Angles		
N(1)−Mg(1)−N(2)	86.7(3)		N(3)−Mg(1)−C(15)	111.1(3)
N(1)−Mg(1)−N(3)	136.7(3)		N(4)−Mg(1)−C(15)	106.4(3)
N(1)−Mg(1)−N(4)	80.8(3)		O−Mg(2)−C(21)	100.2(3)
N(1)−Mg(1)−C(15)	112.1(3)		O−Mg(2)−C(27)	105.8(3)
N(2)−Mg(1)−N(3)	79.9(3)		O−Mg(2)−C(33)	103.9(3)
N(2)−Mg(1)−N(4)	148.1(3)		C(21)−Mg(2)−C(27)	113.0(3)
N(2)−Mg(1)−C(15)	105.5(3)		C(21)−Mg(2)−C(33)	113.8(3)
N(3)−Mg(1)−N(4)	89.2(3)		C(27)−Mg(2)−C(33)	117.7(3)

second liquid phase encountered with preparations using other R$_2$Mg compounds. Representative results are summarized in Table 3. ^{1}H NMR spectra of solutions prepared with a Hex$_2$-Mg/211C ratio of 2 indicate quantitative formation of HexMg-(211C)$^+$ and Hex$_3$Mg$^-$.[3] Key features are (1) two sets of hexyl absorptions in 3/1 ratio, (2) the smaller CH$_2$Mg absorption at much higher field (δ −0.73) than that of Hex$_2$Mg (δ 0.20), and (3) cryptand absorptions considerably more complex than those of uncoordinated cryptand.[20] When the Hex$_2$Mg/211C ratio is less than 2, the same absorptions remain, but are accompanied

Table 3. ^{1}H NMR Observations of Benzene-d_6 Solutions Prepared from (Hexyl)$_2$Mg and Cryptands

cryptand	initial[a] [Hex$_2$Mg]:[C]	^{1}H NMR, δ CH$_2$Mg$^-$	CH$_2$MgC$^+$	[CH$_2$Mg$^-$]/ [CH$_2$MgC$^+$][b]	free C present	initial [C]
	∞	0.20				0
211C	1.0	0.02	−0.73	2.9	yes	0.069
211C	1.3	0.02	−0.73	3.1	yes	0.069
211C	2.4	0.03	−0.74	3.7	no	0.055
211C	3.4	0.14	−0.77	5.8	no	0.043
211C	5.7	0.16	−0.79	10.3	no	0.035
221C	0.5	−0.03	−0.66	5.3	yes	0.03
221C	1.0	0.04	−0.64	5.0	yes	0.08
221C	1.5	0.07	−0.65	5.5	yes	0.10
221C	2.4	0.13	−0.65	6.0	yes	0.06
221C	2.8	0.15	−0.66	5.5	no	0.06
221C	3.3	0.13	−0.66	4.9	no	0.06
221C	5.7	0.10	−0.70	8.4	no	0.06
221C	7.0[c]	0.12	d		no	0.05
221C	9.0[c]	0.12	d		no	0.03
222C	0.7	0.09	−0.55	e	yes	0.05
222C	1.7	0.14	−0.57	7.1	yes	0.05
222C	2.0	0.15	−0.57	7.0	yes	0.05
222C	3.9	0.12[f]	−0.57	14	yes	0.04
222C	6.0	0.15[f]	−0.55	22	yes	0.03
222C	6.7	0.13[f]	−0.55	35	yes	0.02

^{a} Determined from areas of hexyl and cryptand absorptions except where noted. The areas of CH$_2$Mg and CH$_3$ absorptions of hexyl groups could be determined, but the absorptions of their (CH$_2$)$_4$CMg groupings and some cryptand absorptions overlapped. From the hexyl absorptions (CH$_3$ and CH$_2$Mg) that could be determined, the areas of the others ((CH$_2$)$_4$CMg) were calculated and then subtracted from the overlapping absorptions of cryptand and (CH$_2$)$_4$CMg to give the areas of cryptand absorptions. ^{b} Determined from areas of CH$_2$Mg absorptions. ^{c} Ratio of amounts used in the preparation. ^{d} Not detected in the NMR spectra. ^{e} CH$_2$Mg$^+$ absorption too small for meaningful area determination. ^{f} This absorption was broad.

by absorptions of free cryptand. When the ratio exceeds 2, the absorptions attributed to HexMg(211C)$^+$ are unchanged, but the other CH$_2$Mg absorption is broader and its position shifted toward that of free Hex$_2$Mg. The results indicate that the equilibrium constant for the process in eq 2 (R = hexyl) is sufficiently large that essentially all Hex$_2$Mg is incorporated

$$2R_2Mg + cryptand \rightleftharpoons RMg(cryptand)^+ + R_3Mg^- \quad (2)$$
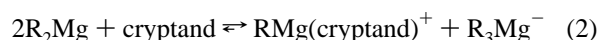
into HexMg(211C)$^+$ and Hex$_3$Mg$^-$ when sufficient 211C is present.[3] Besides the hexyl absorptions assigned to HexMg-(211C)$^+$, only one other set of hexyl absorptions is ever seen; when Hex$_2$Mg/211C exceeds 2, the hexyl groups of excess Hex$_2$-Mg either exchange with those of Hex$_3$Mg$^-$ or are incorporated into a larger ion (whose hexyl groups become equivalent relative to the NMR time scale).

The CH$_2$Mg absorption of the cation is the AA′ portion of an AA′XX′ system; this pattern,[21] due to coupling to the CH_2-CH$_2$Mg hydrogens, indicates that each CH$_2$Mg hydrogen retains its stereochemical integrity for a period that is long relative to the NMR time scale. The larger CH$_2$Mg absorption, by contrast, never exhibits an AA′XX′ pattern; it is a triplet when Hex$_2$-Mg/211C is 2 and broadens as this ratio is increased until ultimately the triplet structure disappears. Therefore, configurations of hexyl groups not in the cation are not maintained, and these hexyl groups must exchange relatively rapidly. NMR spectra of a toluene-d_8 solution of composition HexMg(211C)$^+$-

(20) Reproductions of ^{1}H NMR spectra of NpMg(211C)$^+$ and TolMg-(221C)$^+$ are available.[1,2]

(21) Some observations of AA′XX′ spectra for RCH$_2$CH$_2$Mg compounds: Whitesides, G. M.; Witanowski, M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 2854. Whitesides, G. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4878. Witanowski, M.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 737. Hanawalt, E. M.; Farkas, J., Jr.; Richey, H. G., Jr. *Organometallics* **2004**, *23*, 416.

Hex$_3$Mg$^-$ were taken at lower temperatures. The CH$_2$Mg absorption of the cation was not significantly broader at -80 °C (width at half-height increased only from 23 Hz at 20 °C to 24 Hz at -80 °C), but that absorption of the anion broadened significantly (width at half-height increased from 28 Hz at 20 °C to ca. 106 Hz at -80 °C). One possible explanation is that lower temperatures slow equilibration of the R groups of an anion that has a structure such as **1** (R = Hex) that is more complex than Hex$_3$Mg$^-$.

For preparations of Hex$_2$Mg and 221C or 222C (Table 3), the general features of the ^{1}H NMR absorptions, including an AA′XX′ pattern for CH$_2$Mg of the cation, were similar to those observed with 211C preparations. A significant difference, however, was that the ratio of HexMg(221C)$^+$ to other hexyl groups never exceeded ca. 1/5, even when the Hex$_2$Mg/221C reactant ratio was as low as 0.5. Absorptions of free cryptand were seen until the (Hex)$_2$Mg/221C ratio exceeded ca. 2.5. The ratio of hexyl groups in HexMg(222C)$^+$ to other hexyl groups never exceeded 1/7; free cryptand was evident even with a Hex$_2$-Mg/cryptand ratio of 7. The absorptions of "free" cryptand were shifted slightly upfield ($\leq$0.2 ppm) from their normal positions in benzene, probably due to routine coordination of heteroatoms of the cryptand to Hex$_2$Mg. The CH$_2$Mg absorption of HexMg-(221C)$^+$ in a toluene-d_8 solution having a 1/5 ratio of that cation to other hexyl groups was not significantly broader at -80 °C (width at half-height increased only from 5 Hz at 20 °C to ca. 6 Hz at -80 °C), but the other CH$_2$Mg absorption broadened significantly (width at half-height increased from 13 Hz to ca. 51 Hz).[22]

Exchange studies confirmed the indication from the results above that 211C is more effective than 221C in converting Hex$_2$-Mg to HexMg(cryptand)$^+$. When 1 equiv of 211C was added to a solution of HexMg(221C)$^+$Hex$_3$Mg$^-$, a ^{1}H NMR spectrum recorded after 10 min indicated the HexMg(211C)$^+$/HexMg-(221C)$^+$ ratio to be ca. 2; after 2 h only HexMg(211C)$^+$ absorptions were evident. When 221C was added to a solution of HexMg(211C)$^+$Hex$_3$Mg$^-$, NMR absorptions of HexMg-(221C)$^+$ were not detected even after one week.

^{1}H NMR spectra of freshly prepared Hex$_2$Mg–cryptand solutions were almost free of absorptions not attributable to the species discussed above (and to small amounts of hexane). The solutions were reasonably stable over time, although a slow reaction was noted in some solutions. Np$_2$Mg–211C solutions had earlier been found[23] to undergo a slow cleavage of a short bridge of the cryptand to produce an $-$NCH$=$CH$_2$ grouping. Hex$_2$Mg–211C solutions were found to undergo a similar cleavage. With a solution prepared with a Hex$_2$Mg/211C ratio of 3, for example, $-$NCH$=$CH$_2$ absorptions[24] were detected after 24 h; even after 2 weeks, however, these absorptions were small. Cleavage of the cryptand in Hex$_2$Mg–221C solutions was even slower and in Hex$_2$Mg–222C solutions was not detected even after many weeks.

Cryptands and Other Diorganomagnesium Compounds in Benzene. Many preparations with other R$_2$Mg compounds, unlike those with Hex$_2$Mg, had limited solubility or two liquid phases. The primary compound NeoHex$_2$Mg (NeoHex = Me$_3$-CCH$_2$CH$_2$) is much less soluble in benzene than is Hex$_2$Mg,

and its preparations with cryptands also had low solubilities. ^{1}H NMR spectra of the preparations had the same features as hexyl preparations, however, including AA′BB′ absorptions for CH$_2$CH$_2$Mg(221C)$^+$ and an increasing ratio of "other" R absorptions to RMg(cryptand)$^+$ absorptions in the series 211C < 221C < 222C. Np$_2$Mg and 221C (2/1) in benzene formed solutions with ^{1}H NMR absorptions similar to those observed[1] for NpMg(211C)$^+$Np$_3$Mg$^-$, but the ratio of "other" neopentyl absorptions to NpMg(221C)$^+$ absorptions was $\geq$ ca. 5.[25]

s-Bu$_2$Mg, a secondary compound, is soluble in benzene, but preparations with 211C or 221C led to extensive precipitation and NMR spectra of the solutions had significant butane absorptions. Absorptions that can be assigned to *s*-BuMg-(cryptand)$^+$ were present, however: with 211C, for example, a CHMg(211C)$^+$ absorption at δ -0.95 (and a CHMg absorption at δ ca. 0.2 for other *s*-butyl groups). *t*-Bu$_2$Mg,[26] the only tertiary compound studied, is only slightly soluble in benzene; some dissolved when 211C was present, however, and the preparations exhibited ^{1}H NMR absorptions characteristic of 211C incorporated into RMg(cryptand)$^+$ and absorptions[27] that could be due to *tert*-butyl of *t*-BuMg(211C)$^+$ (δ ca. 0.8) and of another species (δ ca. 1.5). With increasing *t*-Bu$_2$Mg/221C reactant ratios, the spectra had decreasing cryptand absorptions and it was not evident that any *t*-BuMg(221C)$^+$ formed. Apparently *t*-Bu$_2$Mg and the cryptand react, but much of what forms is insoluble. With preparations of either *t*-Bu$_2$Mg or *s*-Bu$_2$Mg and 222C, precipitation was insignificant, but only routine coordination of R$_2$Mg by heteroatoms of the cryptand took place; only single sets of R and cryptand absorptions were evident, and these were shifted only slightly ($\leq$0.2 ppm) from those of the free components.

Tol$_2$Mg is insoluble in benzene, and little solute was in solution when it was stirred with benzene solutions of 211C or 222C. At initial Tol$_2$Mg/221C ratios >3, little solute was in benzene solutions. At ratios <3, the ^{1}H NMR spectrum of the portion that dissolved can be assigned to TolMg(221C)$^+$Tol$_3$Mg$^-$;[2] the ratio of the two sets of *p*-tolyl absorptions was ca. 1/3, even when uncoordinated cryptand was present. *t*-BuPh$_2$Mg (*t*-BuPh = *p-tert*-butylphenyl) is slightly more soluble than Tol$_2$Mg in benzene. Little solute remained in solution when it was stirred with a benzene solution of 0.5 equiv of 211C. ^{1}H NMR spectra of solutions resulting from similar preparations with 221C can be assigned to *t*-BuPhMg(221)$^+$*t*-BuPh$_3^-$. With 222C in benzene, *t*-BuPhMg(222C)$^+$*t*-BuPh$_3$Mg$^-$ formed, but solubility was low, and the solutions also exhibited absorptions of free cryptand unless the *t*-BuPh$_2$Mg/222C reactant ratio exceeded ca. 5.[28]

Macrocycles and Diorganomagnesium Compounds in Ethers or with TMEDA. Preparations in diethyl ether generally led to substantial precipitation; even when some material dissolved, the composition of the solution differed from that of the reactants. Addition of some diethyl ether to benzene solutions containing RMg(macrocycle)$^+$ had little effect, however. Addition, for example, of ca. 15 equiv of diethyl ether to a 0.25 M benzene solution of 2-EtBuMg(14N4)$^+$(2-EtBu)$_3$Mg$^-$

(22) The latter number may be somewhat arbitrary because the peak did not appear to be completely symmetrical. The ratio of the CH$_2$Mg absorption of HexMg(211C)$^+$ to that of the other hexyl groups remained ca. 1/5 at -80 °C.

(23) Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *Organometallics* **1985**, *4*, 1154.

(24) A doublet of doublets at δ ca. 6.05 for $-$NC*H*$=$CH$_2$ is particularly characteristic and not overlapped by other absorptions.

(25) (Benzyl)$_2$Mg is insoluble in benzene and did not dissolve in benzene solutions of 211C, 221C, or 222C.

(26) *t*-Bu$_2$Mg preparations retained some diethyl ether (the solvent used in the preparation of the Grignard reagent); heating under vacuum in an effort to remove all diethyl ether led to decomposition.

(27) The *tert*-butyl group lacks an α-H, so *t*-Bu$_2$Mg–cryptand preparations do not have ^{1}H NMR absorptions in the region free from other absorptions (δ 0 to -1) that has been so useful in ^{1}H NMR observations of solutions prepared with other R$_2$Mg compounds.

(28) ^{1}H NMR spectra of preparations in benzene using (2,4,6-trimethylphenyl)$_2$Mg, which is insoluble in benzene, and 221C showed absorptions only of mesitylene and uncoordinated 211C.

did not cause precipitation or greatly alter the ^{1}H NMR spectrum. Addition of 10 vol % of diethyl ether to 2/1 or 3/1 Hex$_2$Mg−211C or Hex$_2$Mg−221C preparations in benzene did not significantly alter the ratio of HexMg(cryptand)$^+$ absorptions to the other set of hexyl absorptions.

While addition of several equivalents of diethyl ether to an *i*-Bu$_2$Mg−14N4 preparation in benzene (that had *i*-BuMg-(14N4)$^+$*i*-Bu$_3$Mg$^-$ in the lower phase) had no significant effect, addition of just 1 equiv of THF (or of 15C5) resulted in a homogeneous solution; the ^{1}H NMR spectrum indicated that all of the 14N4 remained in *i*-BuMg(14N4)$^+$. As more THF was added, however, absorptions of free 14N4 appeared and those of *i*-BuMg(14N4)$^+$ diminished. *t*-Bu$_2$Mg−14N4 preparations in THF-d_8 were homogeneous; ^{1}H NMR spectra had only single sets of isobutyl absorptions and 14N4 absorptions characteristic of uncoordinated 14N4. Results with an arylmagnesium compound were different. A solution formed by dissolving Tol$_2$Mg and 14N4 (2/1) in THF-d_8 contained TolMg-(14N4)$^+$ and Tol$_3$Mg$^-$; the ^{1}H NMR spectrum exhibited two sets of *p*-tolyl absorptions in ca. 3/1 ratio, and these and the 14N4 absorptions resembled those assigned to TolMg(14N4)$^+$-Tol$_3$Mg$^-$ in preparations in benzene. Similar Tol$_2$Mg−14N4 preparations in diethyl ether were insoluble.[29] Efforts with 211C were hampered by low solubility. A 2/1 Tol$_2$Mg−221C preparation, however, formed TolMg(221C)$^+$ and Tol$_3$Mg$^-$; the ^{1}H NMR absorptions (Figure 5) of the tolyl groups are similar to those in the 14N4 preparation. Some Tol$_2$Mg dissolved in a THF solution of 222C, but the ^{1}H NMR spectrum exhibited only one set of tolyl ^{1}H NMR absorptions and the 222C absorptions were shifted only slightly from those of uncoordinated 222C.

Addition of TMEDA (4 equiv) to a benzene solution of HexMg(211C)$^+$Hex$_3$Mg$^-$ resulted in slow disappearance of HexMg(211C)$^+$. The ratio of the "other" CH$_2$Mg absorption to the CH$_2$Mg(211C)$^+$ absorption increased from 3 to 13 in 4 h and absorptions of uncoordinated cryptand grew correspondingly; after 1 week, HexMg(211C)$^+$ absorptions were negligible. Similar addition of TMEDA to a solution prepared from Hex$_2$-Mg and 221C (2/1) resulted in disappearance of virtually all HexMg(221C)$^+$ in less than 15 min. Coordination of TMEDA to R$_2$Mg (to form R$_2$Mg(TMEDA) is more favorable than formation of RMg(cryptand)$^+$.

Discussion

Only with extraordinary[30] R's are structures of organomagnesium compounds as simple as the formulas such as RMgX or R$_2$Mg that we usually use for them. The magnesium of R$_2$-Mg, for example, ordinarily is bonded to at least four groups.[31] In solvents such as diethyl ether or THF, frequently used with

(29) Tol$_2$Mg is not very soluble in diethyl ether.

(30) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; McGeary, C. A.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **1989**, 273. Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; McGeary, C. A.; Smith, J. D.Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; Kundu, K.; McGeary, C. A.; Smith, J. D. *J. Organomet. Chem.* **1994**, *480*, 199. Wehmschulte, R. J.; Power, P. P. *Organometallics* **1995**, *14*, 3264.

(31) For information about coordination in solutions: Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, l982; Chapter 4. Lindsell, W. E. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, l995; Vol. 1, Chapter 3. Additional evidence now includes information from EXAFS and LAXS techniques: Ertel, T. S.; Bertagnolli, H. In *Grignard Reagents: New Developments*; Richey, H. G., Jr., Ed.; Wiley: Chichester, 2000; Chapter 10. There is abundant evidence for coordination in crystalline solids: Bickelhaupt, F. In *Grignard Reagents: New Developments*; Richey, H. G., Jr., Ed.; Wiley: Chichester, 2000; Chapter 9.
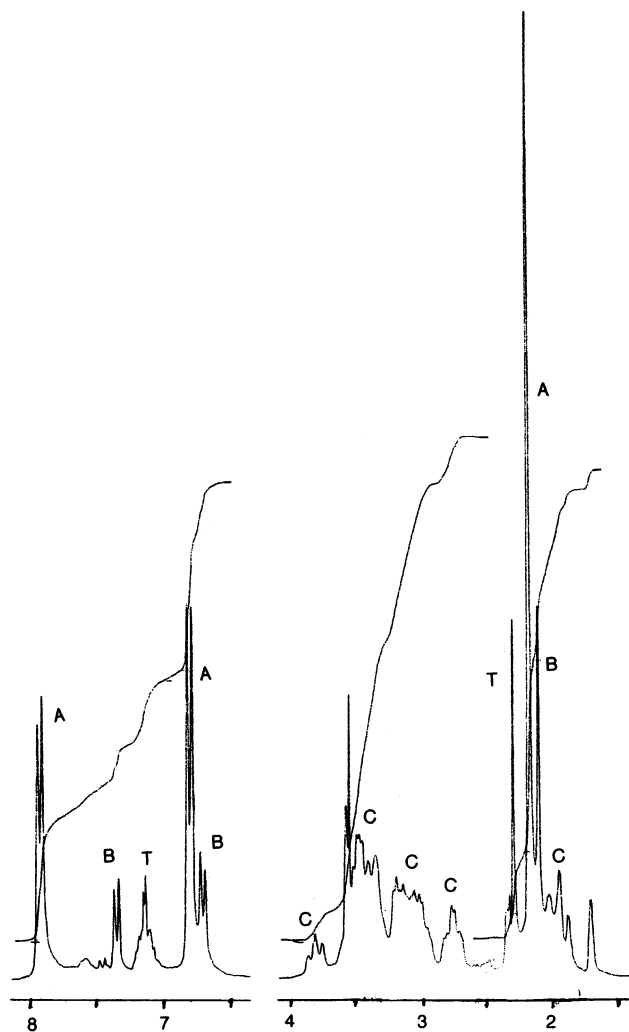

Figure 5. ^{1}H NMR spectrum (200 MHz) of a THF-d_8 solution of TolMg(221C)$^+$Tol$_3$Mg$^-$. Absorptions of the anion are labeled A. Absorptions of the aryl group and 221C of the cation are labeled B and C, respectively. Absorptions of a trace of toluene are labeled T.

these reagents, the oxygen atoms of two or more solvent molecules are usually bonded to the magnesium. In the absence of such solvents, R groups may be bonded in a bridging fashion to two magnesium atoms. The thirst of the magnesium of an organomagnesium compound to form several bonds is evident in the results reported in this paper.

Extent of RMg(macrocycle)$^+$ Formation. Three factors are obviously important in determining how effectively R$_2$Mg is converted to RMg(macrocycle)$^+$.

1. Macrocycle. Many combinations in benzene of R$_2$Mg compounds and 14N4, 211C, 221C, or 222C (where low solubility was not a limitation) produced solutions containing some RMg(macrocycle)$^+$.[32] Transformation of a given R$_2$Mg to RMg(macrocycle)$^+$ was greatest with 14N4 and 211C, less with 221C, and least with 222C. When the R$_2$Mg/macrocycle ratio was 2, all R groups in benzene solutions with 14N4 or 211C were in RMg(macrocycle)$^+$R$_3$Mg$^-$. When R was alkyl, the ratio of RMg(221C)$^+$ to "other" R's usually was ≤1/5; the ratio of RMg(222C)$^+$ to "other" R's was even lower, and with some R's, RMg(222C)$^+$ was not detected.

(32) Conversion of R$_2$Mg to RMg(macrocycle)$^+$ probably is very rapid. Equilibrium always had been reached by the time of the first NMR observation (in some instances only 5−10 min after preparation).

Formation of a multitude of magnesium−heteroatom bonds must be responsible for the conversion of R_2Mg to $RMg(macrocycle)^+$. Indeed, the magnesium of RMg^+ can form bonds of relatively normal lengths[1] to all O and N atoms of 211C, but its two organic groups will prevent an R_2Mg compound from forming many bonds with 211C. A study[33] that measured the abilities of macrocycles to coordinate to $NpMg^+$ found the relative abilities of 211C, 221C, and 14N4 to be 180:1.2:1. In this work, however, 221C was significantly less effective than 14N4 and 211C in converting R_2Mg to $RMg(macrocycle)^+$. The extent of formation of $RMg(macrocycle)^+$ does not necessarily parallel the relative abilities of macrocycles to coordinate to RMg^+ since the effect of this coordinating ability *will be reduced* by the ability of the macrocycle to coordinate to intact R_2Mg (e.g., eq 1). Note that excess 14N4 reduced the formation of $HexMg(14N4)^+Hex_3Mg^-$, presumably by coordinating to Hex_2Mg, but excess 211C did not reduce the formation of $HexMg(211C)^+Hex_3Mg^-$; the relatively rigid geometry of 211C may prevent it from providing coordination to Hex_2Mg as effective as that available from 14N4. Because of their larger "cavities", 221C and 222C are less effective than 211C in forming an array of bonds to RMg^+ (but perhaps more effective in forming two or more bonds to R_2Mg). TMEDA does not with R_2Mg compounds form detectable amounts of $RMg(TMEDA)^+$ ions, but does convert solutions of $HexMg(211C)^+$ or $HexMg(221C)^+$ and accompanying anions to Hex_2Mg coordinated with TMEDA.

2. Solvent.[34] $RMg(macrocycle)^+$ formation tends to be less favorable in THF than in benzene. 2-$EtBu_2Mg$ or i-Bu_2Mg, for example, formed $RMg(14N4)^+$ in benzene but not in THF, and addition of some THF to an i-$BuMg(14N4)^+i$-Bu_3Mg^- preparation in benzene resulted in reduced amounts of the ions and appearance of uncoordinated 14N4. Coordination of these R_2Mg compounds by THF must be more favorable than the disproportionation that forms $RMg(14N4)^+$.

3. R Group. Formation of $RMg(macrocycle)^+$ was more favorable with the aryl groups that were studied than with alkyl groups. Tol_2Mg and t-$BuPh_2Mg$ were the only R_2Mg compounds to form benzene solutions having a 1/3 ratio of $RMg(221C)^+$ to other R's, and Tol_2Mg was the only R_2Mg compound to form $RMg(221C)^+$ in THF. Disproportionation of R_2Zn−macrocycle systems also is more favorable for aryl than alkyl groups, and a study[33] indicated that the more favorable disproportionation with aryl groups is due principally to enhanced stability of the anion rather than of the cation. The observation that no cation formed from 222C and s-Bu_2Mg or t-Bu_2Mg suggests an adverse steric effect on stability of s-$BuMg(222C)^+$ or t-$BuMg(222C)^+$ or the accompanying anions, an effect not sufficient to prevent formation of the corresponding cations with the more potent 211C.

Nature of $RMg(macrocycle)^+$. ^{1}H NMR absorptions of these ions are generally sharp, indicating that their R groups do not exchange with R groups of other species in the solutions at rates significant relative to the NMR time scale. The AA′XX′ ^{1}H NMR pattern observed for $CH_2CH_2Mg(macrocycle)^+$ groupings indicates the absence of processes that rapidly invert the α-carbon. When "free" macrocycle was present in a solution, it did not exchange significantly (relative to the NMR time scale) with the macrocycle of $RMg(macrocycle)^+$.

Nature of Anion. To fully define structures of anions in the solutions will require more investigation. The ratio of the "other" R groups to $RMg(macrocycle)^+$ ranged from 3 to much larger numbers, though these "other" groups afforded only a single set of ^{1}H NMR absorptions. When the anion composition is R_3Mg^-, the structure could be a magnesium bonded equally to three R groups, as in solid $NpMg(211C)^+Np_3Mg^-$. Alternatively, it could be a dimer (**1**), as in solid $EtMg(221C)^+Et_3Mg^-$, though the observation of only one set of NMR absorptions for R then would indicate that interchange of the two structurally different types of R groups (probably by dissociation to R_3Mg^- followed by recombination) is rapid relative to the NMR time scale. Low temperatures would slow exchange and might permit seeing two sets of R absorptions. Most efforts to take spectra at significantly lower temperatures were not meaningful because solubility became too low, but with a (toluene-d_8) solution of composition $HexMg(211C)^+Hex_3Mg^-$, the CH_2Mg absorption of the anion but not of the cation broadened significantly at lower temperature. When the ratio of "other" R groups to $RMg(macrocycle)^+$ exceeds 3, either the R groups of R_3Mg^- and R_2Mg exchange rapidly or an anion larger than R_3Mg^- (and whose R groups equilibrate rapidly) is present.[35]

A donor molecule (D) with an O or N atom must sometimes coordinate to the anion (as in $Ph_3Mg(THF)^-$ in the crystal structure (Figure 4)). Addition of 1 equiv of THF or 15C5 to an i-Bu_2Mg−14N4 preparation in benzene that had i-$BuMg(14N4)^+i$-Bu_3Mg^- in the lower phase resulted in a homogeneous solution that still had only the absorptions attributed to i-$BuMg(14N4)^+$ and an anion. The THF most likely promoted solubility by forming i-$Bu_3Mg(THF)^-$. Similarly, a small amount of THF solubilized methallyl$(14N4)^+$(methallyl)$_3Mg^-$ and $Xyl(14N4)^+Xyl_3Mg^-$.[36]

Experimental Section

General Procedures. Procedures involving organometallic compounds were performed under an atmosphere of purified nitrogen using Schlenk techniques, a glovebox, and a vacuum line. NMR spectra were recorded at ca. 23 °C except where noted. ^{1}H NMR absorption positions for benzene-d_6 solutions are relative to internal C_6D_5H (δ 7.15) and for THF-d_8 solutions to internal $CHDCD_2O$ (δ 1.73). Solutions for NMR analysis were prepared in a glovebox and transferred into NMR tubes to which an extension of routine glass tubing had been added to facilitate sealing with a flame. An NMR tube was capped temporarily with a septum, removed from the glovebox, immersed in liquid nitrogen, and sealed at the extension.

Supporting Information Available: Experimental information including purification of reagents, syntheses of R_2Mg compounds, NMR data for representative R_2Mg−macrocycle combinations, and details of the X-ray structure determination. This material is available free of charge via the Internet at http://pubs.acs.org.

(33) Tang, H.; Parvez, M.; Richey, H. G., Jr. *Organometallics* **2000**, *19*, 4810.

(34) Formation of a second liquid phase, sometimes observed when benzene was the solvent, seemed to be favored by an R that was small and by an R_2Mg/macrocycle ratio of ca. 2, corresponding to a solute composition of $RMg(cryptand)^+R_3Mg^-$.

(35) A ratio of "other" R groups to $RMg(macrocycle)^+$ of ca. 5 was encountered frequently. Perhaps a particular stability is associated with this ratio, with the consequence that additional macrocycle does not always convert $R_5Mg_2^-$ to R_3Mg^-. A ratio of 5 was found in solid $MeMg(15-crown-5)^+Me_5Mg_2^-$ (the anion is polymeric).[8]

(36) Enhanced solubility of $TolMg(14N4)^+Tol_3Mg^-$ when excess 14N4 was present may have been due to coordination of the magnesium of the anion to a nitrogen of excess 14N4.