Articles

Preparation and Properties of RMg(macrocycle)$^+$ Cations with Accompanying Anions Derived from Acidic Hydrocarbons or a Hindered Phenol

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Reactions of an R_2Mg compound, a macrocycle, and fluorene (FlH) or indene (InH) can form RMg(macrocycle)$^+$ and Fl$^-$ or In$^-$. Some reactions of RMgOAr (Ar = 2,6-di-*tert*-butylphenyl) and macrocycles form RMg(macrocycle)$^+$RMg(OAr)$_2^-$. Crystal structures of MeMg(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)$^+$Cp$^-$, *i*-BuMgOAr(18-crown-6), and EtMgOAr(tetramethylethylenediamine) are reported.

Solutions containing RMg(macrocycle)$^+$ cations have been prepared from reactions of R_2Mg compounds and macrocycles in benzene and ethers (e.g., eq 1).[1−3] To

$$2 \ R_2Mg + \text{macrocycle} \rightarrow$$
$$\text{RMg(macrocycle)}^+ + R_3Me^- \quad (1)$$

enable studies of behavior of RMg(macrocycle)$^+$ cations such as exchange of the macrocycle and interaction with solvents, we wanted to prepare solutions of these cations accompanied by anions that would be much less reactive than organomagnesate anions and that would have minimal interaction with the cations. One obvious approach was to treat a Grignard reagent (RMgX) with a macrocycle to form RMg(macrocycle)$^+$X$^-$. Such reactions tend to form solids, however, and when the products are in solution, the anion frequently is RMgX$_2^-$ or R_2MgX$^-$ instead of X$^-$ and the cation sometimes is XMg(macrocycle)$^+$.[4] An approach investigated in this study is to use conjugate bases of the acidic hydrocarbons cyclopentadiene, indene, and fluorene or of a hindered phenol as counterions for RMg(macrocycle)$^+$.

Results and Discussion

Reactions of RMgCp and Macrocycles. X-ray Structure of MeMg(14N4)$^+$Cp$^-$. Reaction of RMgCp with a macrocycle (eq 2) is a potential pathway to RMg(macrocycle)$^+$ cations. Addition of MeMgCp to a

$$\text{RMgCp} + \text{macrocycle} \rightarrow \text{RMg(macrocycle)}^+\text{Cp}^- \quad (2)$$

solution of 1 equiv of 14N4 (14N4 = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) in benzene resulted in a slurry which, when heated to dissolve the solid and then allowed to cool slowly, provided crystals suitable for X-ray diffraction analysis. The ORTEP drawing (Figure 1) shows MeMg(14N4)$^+$ and Cp$^-$ units. Selected bond distances and bond angles are listed in Table 1. The distance of Mg from the Cp plane (5.19 Å) indicates the absence of significant Mg−Cp bonding; such distances are ca. 2.0−2.2 Å (and Mg−C distances are ca. 2.3−2.4 Å) in magnesocene structures.[5] The magnesium atom is bonded to the four ring nitrogens with similar bond distances (2.21−2.25 Å). The C−Mg bond distance (2.14 Å) is the same as that found[2,6] for the cation MeMg(15C5)$^+$.

The ^{1}H NMR spectrum (Figure 2) of the solid in benzene-d_6 has absorptions characteristic of RMg-(14N4)$^+$ ions.[4,7] CHMg absorptions of such ions are unusually far upfield; the CH$_3$Mg absorption in this case

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* To whom correspondence should be addressed (M.P. particularly for crystal structures of MeMg(14N4)$^+$Cp$^-$ and *i*-BuMgOAr(18C6); R.R.W. particularly for crystal structure of EtMgOAr(TMEDA)). E-mail: parvez@ucalgary.ca; bob.whittle@aai-research.com; hgr@chem.psu.edu.

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(1) Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **l985**, *107*, 432. Richey, H. G., Jr. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D. Vögtle, F., Eds.; Pergamon: Oxford, l996; Vol. 1 (G. W. Gokel, Ed.), Chapter 21. Also see: Viebrock, H.; Behrens, U.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1257.

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

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

(4) Pajerski, A. D.; Chubb, J. E.; Fabicon, R. M.; Richey, H. G., Jr. *J. Org. Chem.* **2000**, *65*, 2231.

(5) Bickelhaupt, F. In *Grignard Reagents: New Developments*; Richey, H. G., Jr., Ed.; Wiley: Chichester, U.K., 2000; Chapter 9.

(6) The accompanying anion is a polymeric chain of composition Me$_5$Mg$_2^-$.

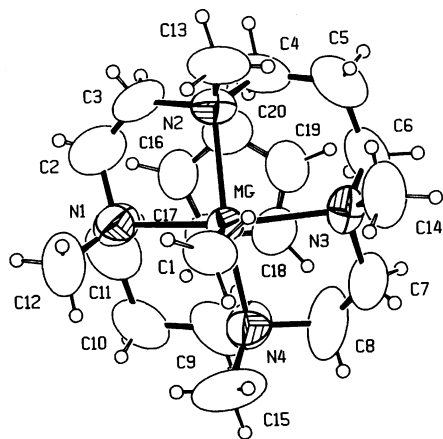(7) Tang, H.; Richey, H. G., Jr. *Organometallics* **2001**, *20*, 1569.

Figure 1. ORTEP drawing of MeMg(14N4)$^+$Cp$^-$. Atoms are shown with 50% probability ellipsoids.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Crystal Structures

MeMg(14N4)$^+$Cp$^-$ (Figure 1)			
Bond Distances			
Mg−N(1)	2.241 (5)	Mg−N(4)	2.235 (5)
Mg−N(2)	2.208 (6)	Mg−C(1)	2.136 (7)
Mg−N(3)	2.252 (5)		
Bond Angles			
N(1)−Mg−N(2)	81.3 (2)	N(2)−Mg−N(4)	140.9 (3)
N(1)−Mg−N(3)	146.5 (2)	N(2)−Mg−C(1)	110.6 (2)
N(1)−Mg−N(4)	88.0 (3)	N(3)−Mg−N(4)	80.6 (2)
N(1)−Mg−C(1)	107.1 (2)	N(3)−Mg−C(1)	106.4 (2)
N(2)−Mg−N(3)	87.9 (2)	N(4)−Mg−C(1)	108.6 (2)
i-BuMgOAr(18C6) (Figure 5)			
Bond Distances			
Mg−O(1)	2.241 (3)	Mg−O(7)	1.895 (3)
Mg−O(2)	2.249 (3)	Mg−C(27)	2.175 (5)
Mg−O(3)	2.161 (3)		
Bond Angles			
O(1)−Mg−O(2)	69.2 (1)	O(2)−Mg−O(7)	90.1 (1)
O(1)−Mg−O(3)	111.8 (1)	O(2)−Mg−C(27)	154.0 (2)
O(1)−Mg−O(7)	127.5 (1)	O(3)−Mg−O(7)	105.4 (1)
O(1)−Mg−C(27)	92.0 (2)	O(3)−Mg−C(27)	101.1 (1)
O(2)−Mg−O(3)	71.42 (9)	O(7)−Mg−C(27)	115.9 (2)
EtMgOAr(TMEDA) (Figure 6)			
Bond Distances			
Mg−O	1.888 (5)	Mg−N(2)	2.240 (7)
Mg−N(1)	2.211 (7)	Mg−C(1E)	2.147 (10)
Bond Angles			
O−Mg−N(1)	114.5 (3)	N(1)−Mg−N(2)	81.5 (3)
O−Mg−N(2)	117.4 (3)	N(1)−Mg−C(1E)	111.6 (4)
O−Mg−C(1E)	116.4 (4)	N(2)−Mg−C(1E)	110.5 (4)

is at δ −1.59. The 14N4 absorptions are more complex than those of free 14N4 and include a downfield absorption (δ 3.05) for 4 hydrogens of the 14N4. ^{1}H NMR absorptions of RMg(14N4)$^+$ cations are relatively insensitive to the anion, except for this low-field absorption, which we have assigned[4,7] to four NC*H*HCH$_2$C*H*HN hydrogens that (as evident in the crystal structure) are on the side of the cation opposite from the R group. The anion accompanying RMg(14N4)$^+$ in solution (as is Cp$^-$ in the crystal structure) must reside most frequently on the side of this cation opposite from R and as close to the Mg as possible, bringing it near to the NC*H*HCH$_2$C*H*HN hydrogens.

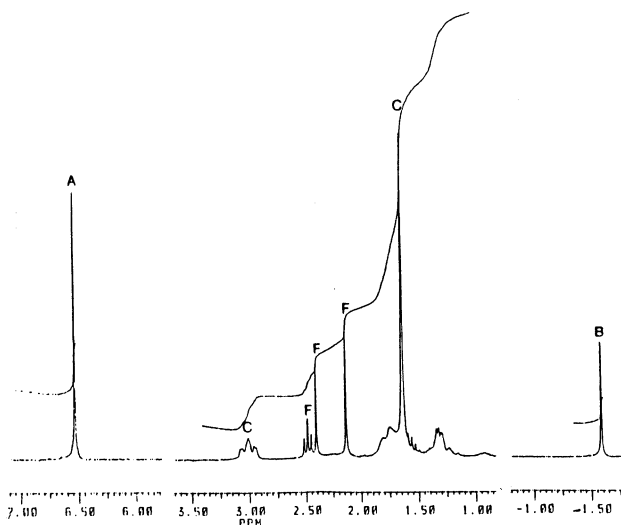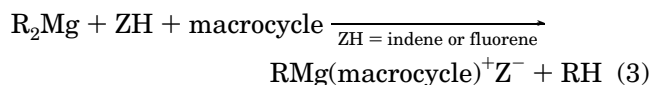^{1}H NMR spectra of 1:1 solutions of 15C5 (15C5 = 15-crown-5) and EtMgCp or *i*-BuMgCp in benzene-d_6 gave

Figure 2. ^{1}H NMR spectrum (200 MHz) of a benzene-d_6 solution of MeMg(14N4)$^+$Cp$^-$. The absorption of the cyclopentadienyl anion is labeled A; the absorption of the methyl group and the absorptions of the 14N4 of MeMg(14N4)$^+$ are labeled B and C, respectively. Some free 14N4 exhibits sharp absorptions, labeled F, indicating that it does not exchange rapidly relative to the NMR time scale with the 14N4 of MeMg(14N4)$^+$.

no evidence for the presence of RMg(15C5)$^+$. When the reactant ratio was ca. 1:2, however, observations (described in the Supporting Information) that include ^{1}H NMR absorptions characteristic[2,3,8] of RMg(15C5)$^+$ suggested formation of RMg(15C5)$^+$RMg(Cp)$_2$$^-$. Investigation of RMgCp reactions was not continued because simpler behavior was found for reactions involving fluorene or indene.

Reactions of R$_2$Mg, a Macrocycle, and Indene or Fluorene. Reactions of R$_2$Mg, a macrocycle, and an acidic hydrocarbon might prepare (eq 3) RMg(macrocycle)$^+$ cations. Prior work had found that the very slow

$$R_2Mg + ZH + macrocycle \xrightarrow{\text{ZH = indene or fluorene}}$$
$$RMg(macrocycle)^+Z^- + RH \quad (3)$$

rate of metalation of fluorene by Et$_2$Mg in diethyl ether is increased greatly (ca. 10^5) by the presence of 15C5 (15-crown-5)[9] and that some reactions in benzene of R$_2$Mg and 1,2,3,4-tetraphenyl-1,3-cyclopentadiene plus a macrocycle form solutions of RMg(macrocycle)$^+$-Ph$_4$C$_5$H$^-$.[8] Organomagnesates (e.g., R$_3$Mg$^-$, eq 1) were thought to be the bases responsible for proton removal.

Reactions of several R$_2$Mg compounds with 15C5, 14N4, or 211C (2,1,1-cryptand) and fluorene (FlH) or indene (InH) did prepare benzene solutions of RMg-(macrocycle)$^+$ cations. Although crystals were obtained in some experiments, none were suitable for X-ray analysis. Fortunately, NMR spectra of solutions definitively indicated formation of RMg(macrocycle)$^+$ and Fl$^-$ or In$^-$. Addition of 15C5 to a diethyl ether solution of fluorene and Et$_2$Mg, *i*-Bu$_2$Mg, (2-EtBu)$_2$Mg (2-EtBu = 2-ethylbutyl), or Np$_2$Mg (Np = neopentyl = (CH$_3$)$_3$CCH$_2$) produced bright orange precipitates,[10] all sufficiently soluble in benzene (benzene-d_6) to permit taking routine

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

(9) Richey, H. G., Jr.; King, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 432.
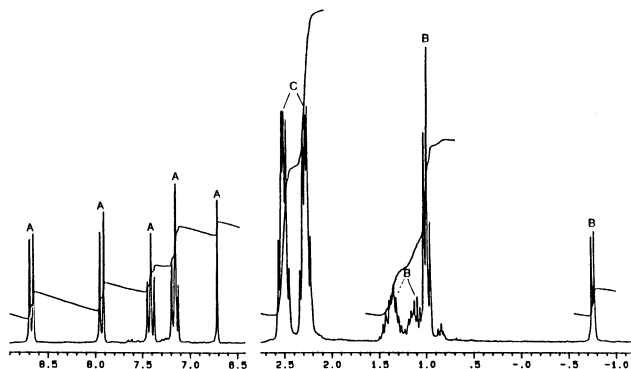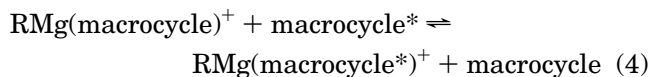
Figure 3. ^{1}H NMR spectrum (200 MHz) of a benzene-d_6 solution of (2-EtBu)Mg(15C5)$^+$Fl$^-$ prepared from (2-EtBu)$_2$-Mg, 15C5, and fluorene. Absorptions of the fluorenyl anion are labeled A, and those of the 2-ethylbutyl group and 15C5 of (2-EtBu)Mg(15C5)$^+$ are labeled B and C, respectively.

^{1}H NMR spectra. The absorptions were those expected for RMg(15C5)$^+$Fl$^-$. The 2-ethylbutyl precipitate was the most soluble, and its spectrum (Figure 3) is typical. The CH$_2$Mg absorption (δ −0.74) is far upfield, and two crown ether absorptions (δ 2.31 and 2.51) exhibiting an AA′BB′ pattern indicate that the two faces of the crown ether are different. The shift upfield of the 15C5 absorption from that of free 15C5 (δ 3.52) is even larger than has been observed with other anions (e.g., R$_3$Mg$^-$), perhaps due to effects of the shielding cone of the fluorenyl ion. The absorptions attributed to the fluorenyl ion are very similar in all RMg(macrocycle)$^+$Fl$^-$ solutions and are similar to those previously reported[11] for this anion. Addition of 14N4 to diethyl ether solutions of fluorene and Et$_2$Mg or i-Bu$_2$Mg also resulted in bright orange precipitates; ^{1}H NMR spectra (benzene-d_6) of these were characteristic of RMg(14N4)$^+$ and Fl$^-$.

Blue-green precipitates, somewhat more soluble in benzene than the corresponding fluorene preparations, resulted from preparations using indene, i-Bu$_2$Mg, and 15C5 or 14N4. ^{1}H NMR absorptions of benzene-d_6 solutions of these solids were characteristic of the indenyl anion[11] and i-BuMg(15C5)$^+$ or i-BuMg(14N4)$^+$. (Methallyl)$_2$Mg (methallyl = CH$_2$=CMe-CH$_2$) was used in an experiment with indene and 14N4. The set of ^{1}H NMR absorptions assigned to (methallyl)Mg(14N4)$^+$, besides an absorption (δ 1.73) for CH$_3$, had discrete, sharp absorptions that we assign to CH$_2$Mg (δ 0.52) and to =CH$_2$ (δ 4.20). The CH$_2$ groups of allylic organomagnesium compounds[12] and indeed allylic compounds of some other metals[13] usually exhibit a common absorption; even when the metal is associated with one of the methylene carbons, exchange of these carbons is rapid relative to the NMR time scale. The absence of rapid

exchange of the methylene carbons, however, is reasonable for (methallyl)Mg(14N4)$^+$ since steric interactions will make it difficult for more than one allylic carbon to be near the magnesium.[14]

Reactions of RMg(Macrocycle)$^+$ Cations. To investigate exchange (eq 4), a different macrocycle was added to a solution of RMg(macrocycle)$^+$In$^-$. A solution

$$\text{RMg(macrocycle)}^+ + \text{macrocycle*} \rightleftharpoons$$
$$\text{RMg(macrocycle*)}^+ + \text{macrocycle} \quad (4)$$

of i-BuMg(15C5)$^+$ to which 1 equiv of 14N4 was added exhibited ^{1}H NMR absorptions only for i-BuMg(14N4)$^+$ and free 15C5 at first observation (24 h). A solution of i-BuMg(14N4)$^+$In$^-$ to which 211C was added showed no change after many days. When, however, a catalytic amount (ca. 0.01 equiv) of i-Bu$_2$Mg was added, the ^{1}H NMR spectrum (recorded after several hours) showed absorptions only for i-BuMg(211C)$^+$ and free 14N4. By contrast, a solution of i-BuMg(211C)$^+$In$^-$ to which 14N4 and a catalytic amount of i-Bu$_2$Mg were added showed no change after many days. These observations are in accord with previous observations[8] that the strength of coordination to RMg$^+$ decreases in the order 211C > 14N4 > 15C5 and that exchange of the macrocycle is promoted by free R$_2$Mg in the solution. When 15C5 was added to a solution of i-BuMg(15C5)$^+$In$^-$, the absorptions of the 15C5 of the cation and of free 15C5 were broad, indicating that the rate of their exchange became significant relative to the NMR uncertainty time, another suggestion that the equilibrium constant for formation of RMg(macrocycle)$^+$ is significantly less with 15C5 than with 14N4 or 211C.[15,16] ^{1}H NMR spectra indicated that addition of pyridine to a solution of i-BuMg(15C5)$^+$In$^-$ formed i-Bu$_2$Mg (coordinated by pyridine) and free 15C5; the absence of significant indene absorptions indicated that the precipitate that formed was In$_2$Mg. By contrast, pyridine added to a solution i-BuMg(14N4)$^+$In$^-$ remained as free pyridine and no precipitate formed. These results also indicate that coordination of RMg$^+$ is stronger by 14N4 than by 15C5.

Reactions of RMgOAr and Crown Ethers. X-ray Structure of i-BuMgOAr(18C6). 2,6-Di-*tert*-butylphenol (ArOH) was chosen as the phenol because its size

(10) Reactions proceeded more rapidly when R$_2$Mg was in slight excess (e.g., 10%) over macrocycle. This may be due to significant incorporation of R$_2$Mg into R$_2$Mg rotaxanes: refs 2 and 3; Pajerski, A. D.; BergStresser, G. L.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 4844. Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Organometallics*, **1994**, *13*, 2616, and references therein.
(11) Grutzner, J. B.; Lawlor, J. M.; Jackman, L. M. *J. Am. Chem. Soc.* **1972**, *94*, 2306, and references therein.
(12) 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.; Rufińska, A. *J. Organomet. Chem.* **1985**, *293*, 1. Lehmkuhl, H.; Mehler, K.; Benn, R.; Rufińska, A.; Krüger, C. *Chem. Ber.* **1986**, *119*, 1054.
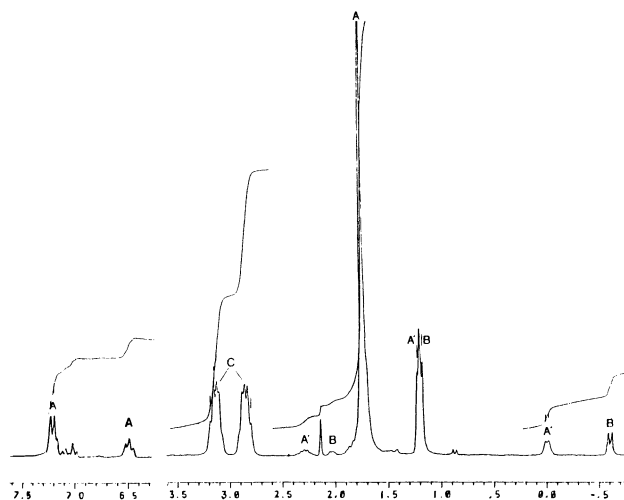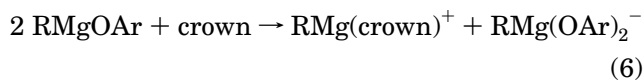
(13) Methallylzinc compounds, for example: Thiele, K.-H.; Engelhardt, G.; Köhler, J.; Arnstedt, M. *J. Organomet. Chem.* **1967**, *9*, 385. Benn, R.; Hoffmann, E. G.; Lehmkuhl, H.; Nehl, H. *J. Organomet. Chem.* **1978**, *146*, 103. Also see: Benn, R.; Grondey, H.; Lehmkuhl, H.; Nehl, H.; Angermund, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1279.
(14) Separate absorptions are not seen for the =C*H*H and =CH*H* hydrogens. These absorptions may be too similar in position to be resolved or, alternatively, may be close enough in position to be averaged by an exchange too slow to affect the more widely separated CH$_2$Mg and =CH$_2$ absorptions.
(15) Broadening of absorptions was less pronounced when 15C5 was added to solutions of 2-EtBuMg(15C5)$^+$ or NpMg(15C5)$^+$; exchange may be slower because the R groups are bulkier.
(16) Addition of 12C4 (12-crown-4) or 18C6 to solutions of i-BuMg-(15C5)$^+$In$^-$ led to substantial precipitation. The composition of i-BuMg-(crown)$^+$ cations in the remaining solutions was not determined because the ^{1}H NMR absorptions of free 12C4, 15C5, and 18C6 were broad and essentially identical, as were the absorptions of 12C4, 15C5, and 18C6 incorporated into RMg(macrocycle)$^+$. In other experiments, it was observed that addition of 12C4 or 18C6 to solutions of i-Bu$_2$Mg and indene led to precipitation of most of the solute. When 14N4 was added to suspensions of these solids, however, the solids dissolved and the ^{1}H NMR spectra of the resulting solutions showed them to contain i-BuMg(14N4)$^+$ and free 12C4 or 18C6.

Figure 4. ^{1}H NMR spectrum (200 MHz) of *i*-BuMg-(18C6)$^+$*i*-BuMg(OAr)$_2^-$ in the lower phase of a preparation of *i*-BuMgOAr and 18C6 (ca. 2:1) in benzene-d_6. Absorptions of the aryl ring and isobutyl group of *i*-BuMg(OAr)$_2^-$ are labeled A and A′, respectively. Absorptions of the isobutyl group and 18C6 of *i*-BuMg(18C6)$^+$ are labeled B and C, respectively.

might promote solubility and its ortho *tert*-butyl groups diminish the tendency of RMgOAr to aggregate.[17] The RMgOAr reactants were synthesized by reactions of ArOH and R$_2$Mg in diethyl ether.[17,18] The results described below indicate that addition of crown ethers to benzene solutions of composition RMgOAr could furnish RMg(crown)$^+$ cations; the accompanying anion, however, never was OAr$^-$ (eq 5) but in many instances clearly was RMg(OAr)$_2^-$ (eq 6). Indeed, when equimolar

$$\text{RMgOAr} + \text{crown} \not\rightarrow \text{RMg(crown)}^+ + \text{OAr}^- \quad (5)$$

$$2\,\text{RMgOAr} + \text{crown} \rightarrow \text{RMg(crown)}^+ + \text{RMg(OAr)}_2^- \quad (6)$$

amounts of reactants were used, one-half of the crown ether remained as "free" crown ether. The studies were complicated when benzene was the solvent by the frequent presence of two liquid phases,[19] the denser containing a substantial portion of the solute. Reactant concentrations ordinarily were 0.5−1.0 M, but two phases also were present at lower concentrations. Rapid separation of significant amounts of solid before NMR spectra could be recorded also was a problem with many preparations.

Reactions of 2:1 amounts of *i*-BuMgOAr and 18C6 in benzene resulted in two liquid phases. The ^{1}H NMR spectrum of a lower phase (Figure 4) shows *two equal sets* of isobutyl absorptions. The AA′BB′ absorption at ca. δ 3.0 that is typical for 18C6 when the two sides of this crown ether are different and the position of the CH$_2$Mg absorption (δ −0.62) suggest that the 18C6 and one isobutyl group are in *i*-BuMg(18C6)$^+$. Similar results were obtained with 2-EtBuMgOAr and 18C6.

(17) Asbhy, E. C.; Nackashi, J.; Parris, G. E. *J. Am. Chem. Soc.* **1975**, *97*, 3162.

(18) Ashby, E. C.; Willard, G. F. *J. Org. Chem.* **1978**, *43*, 4094.

(19) Formation of two phases is often observed with organometallic ions in aromatic solvents. Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic: London, 1984; Vol. 1, Chapter 9.
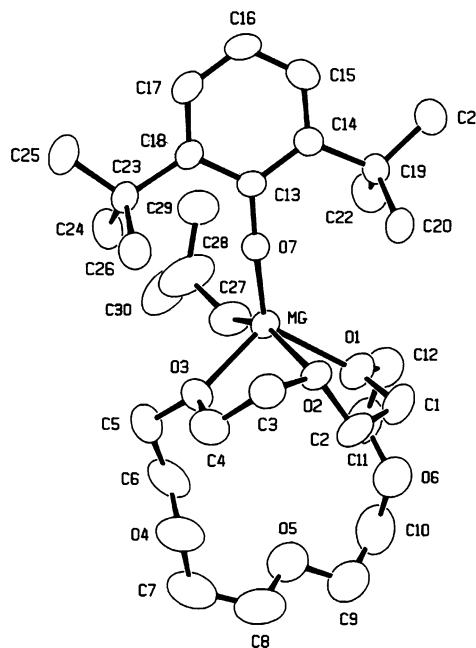

Figure 5. ORTEP drawing of *i*-BuMgOAr(18C6). Atoms are shown with 50% probability ellipsoids.

Precipitation was rapid from similar 1:1 preparations, however, but in the isobutyl case, a ^{1}H NMR spectrum was recorded before precipitation and was very different from that of a 2:1 preparation. The spectrum exhibited only a single set of isobutyl absorptions (the CH$_2$Mg absorption at a routine position, δ 0.08) and the 18C6 absorption was a singlet (δ 3.38). It is probable that the species in solution is *i*-BuMgOAr(18C6) in which magnesium is coordinated in a routine fashion (e.g., **1**) by only two or three crown ether oxygens which exchange rapidly relative to the NMR time scale.

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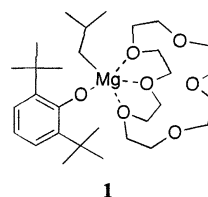
Although the structure of a precipitate need not be similar to that of a dominant species in the solution, it is notable that X-ray analysis of crystals obtained from a 1:1 *i*-BuMgOAr−18C6 preparation also found structure **1**. Recrystallization of the solid that precipitated from a benzene solution prepared from equimolar amounts of *i*-BuMgOAr and 18C6 gave crystals suitable for single-crystal X-ray analysis. Magnesium in the structure (ORTEP drawing in Figure 5, also see **1**) is bonded in a highly distorted pentagonal bipyramidal arrangement to the isobutyl α-carbon, the aryloxy oxygen, and three crown ether oxygens. Selected bond distances and bond angles are listed in Table 1. The Mg−O and Mg−C distances are in normal ranges, but the O−Mg−O bond angles (69.2° and 71.4°) for pairs of nearest neighbor oxygens of the 18C6 are particularly small.

A 2:1 *i*-BuMgOAr−15C5 preparation also resulted in two phases; the ^{1}H NMR spectrum of the lower phase was almost identical to that of the corresponding 18C6

preparation, indicating formation of *i*-BuMg(15C5)$^+$ and *i*-BuMg(OAr)$_2^-$. The ^{1}H NMR spectrum of the lower phase of a 1:1 preparation, however, was very different from that of corresponding 18C6 preparations: the two isobutyl absorptions were virtually identical to those in the spectrum of a 2:1 preparation; only the 15C5 absorption—larger, broader, and nearly featureless—was significantly different. It is likely that *i*-BuMg(15C5)$^+$ and *i*-BuMg(OAr)$_2^-$ are the principal ions (eq 6) at either reactant ratio. When 15C5 is in excess, one-half of the 15C5 is present as free 15C5 but exchanges fairly rapidly relative to the NMR time scale with the 15C5 incorporated into *i*-BuMg(15C5)$^+$. When R was Et or 2-EtBu, 1:1 and 2:1 R$_2$Mg−15C5 preparations also exhibited quite different spectra.[20] With all alkyl groups studied, precipitation from the solutions occurred soon if the R$_2$Mg/15C5 ratio was near 2; solubilities of (*p*-tolyl)MgOAr−15C5 preparations were low at all reactant ratios.

Although 15C5 forms RMg(15C5)$^+$ at an RMgOAr/15C5 reactant ratio of 1 (leaving excess 15C5 in solution), 18C6 performs a similar transformation only at a reactant ratio of 2. The presence of more 18C6 than necessary to form RMg(18C6)$^+$RMg(OAr)$_2^-$ results instead in a species (**1**) that incorporates all of the 18C6. The contrasting behavior of 15C5 and 18C6 can again be attributed to a greater propensity of 15C5 to bond to RMg$^+$.

When diethyl ether rather than benzene was the solvent, combinations of 15C5 and several RMgOAr compounds (R = Me, Et, *i*-Bu, Np, 2-EtBu), all of which are soluble in that solvent, led to precipitates. An experiment using THF-*d*$_8$ as the solvent and 1:1 (*p*-tolyl)-MgOAr and 15C5 resulted in a homogeneous solution whose ^{1}H NMR spectrum indicated formation of (*p*-tolyl)Mg(15C5)$^+$(*p*-tolyl)Mg(OAr)$_2^-$. The spectrum exhibited, for example, two equal sets of tolyl absorptions and two equal crown ether absorptions, one a singlet, the other having an AA′BB′ pattern.

X-ray Structure of EtMgOAr(TMEDA). Reactions in diethyl ether of the phenol and an equimolar amount of Et$_2$Mg or Np$_2$Mg followed by removing the solvent gave a white solid that could be sublimed. The sublimed solids were slightly soluble in benzene; absorption areas in ^{1}H NMR spectra indicated the composition RMgOAr, but the number of absorptions indicated the presence of more than one species. Solubility was much greater when TMEDA was added. When more than 1 equiv of TMEDA was present, two sets of TMEDA absorptions were observed: one set (δ 1.58 and 1.90) was assigned to complexed TMEDA (absorption areas indicated one such TMEDA for each RMgOAr); the absorptions (δ 2.11 and 2.35) of the other set were characteristic of free TMEDA in benzene.[21] Therefore, free TMEDA and TMEDA bound to RMgOAr do not exchange rapidly relative to the NMR time scale.

Crystals suitable for X-ray structural analysis were obtained from a benzene solution of EtMgOAr and TMEDA. As evident in the ORTEP drawing (Figure 6), magnesium is bonded to the α-carbon of an ethyl group,
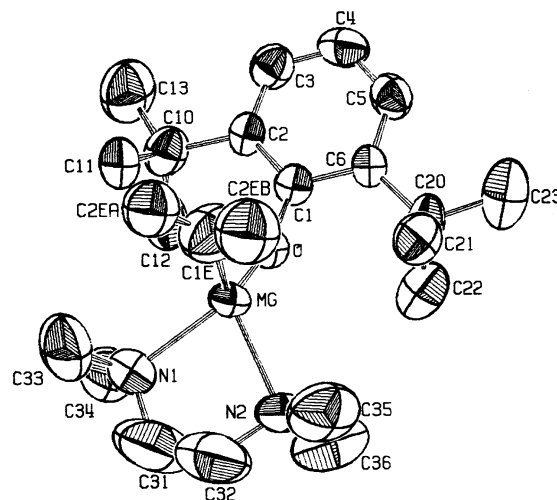

Figure 6. ORTEP drawing of EtMgOAr(TMEDA). Atoms are shown with 50% probability ellipsoids.[22]

the oxygen of OAr, and the two nitrogens of TMEDA.[22] The bond angles (Table 1) at magnesium involving the oxygen of the OAr group exceed the tetrahedral value (O−Mg−N = 114.5° and 117.4°), but as found[5] for several R$_2$Mg(TMEDA) compounds and for Ph$_2$Mg-(TMEDA) and also[23] recently for (ArO)$_2$Mg(TMEDA), the N−Mg−N angle is considerably less (81.5°). The C−Mg−N angles (110.5° and 111.6°) are close to tetrahedral.

Conclusions. Reactions of R$_2$Mg and FlH or InH with some macrocycles lead to RMg(macrocycle)$^+$ and Fl$^-$ or In$^-$. That NMR absorptions of the anions are so similar when accompanied by different RMg(macrocycle)$^+$ cations suggests that there is little specific cation−anion interaction. Studies of exchange of the macrocycle of RMg(macrocycle)$^+$ indicate that effectiveness of coordination to RMg$^+$ decreases in the order 14N4 > 211C > 15C5 > 18C6. Reactions of RMgOAr with macrocycles do not form RMg(macrocycle)$^+$OAr$^-$. Instead, reactions with 15C5 or even with the particularly effective 14N4 lead to RMg(macrocycle)$^+$RMg-(OAr)$_2^-$. With 18C6, formation even of RMg(18C6)$^+$RMg-(OAr)$_2^-$ is marginal, observed when the RMgOAr/18C6 ratio is 2; when that ratio is 1, however, the principal species is RMgOAr(18C6), in which the magnesium is coordinated in a routine fashion by several oxygens of the crown ether.

Experimental Section

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 in benzene-*d*$_6$. ^{1}H NMR absorption positions are relative to internal C$_6$D$_5$H (δ 7.15). 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.

(20) A 1:1 PrMgOAr−15C5 preparation in benzene (2 equiv of THF had been used to solubilize the PrMgOAr) did not separate into two phases and also gave a spectrum assigned to RMg(15C5)$^+$RMg(OAr)$_2^-$.

(21) Two sets of TMEDA absorptions also were seen in ^{13}C NMR spectra, one set having positions of free TMEDA.

(22) The methyl carbon of the ethyl group is disordered; it is shown in Figure 6 as two 50% probability ellipsoids (labeled C2EA and C2EB).

(23) Henderson, K. W.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E.; Parkinson, J. A.; Sherrington, D. C. *Dalton Trans.* **2003**, 1365.

NMR Spectra of Preparations from RMgCp or RMgOAr and Macrocycles. The RMgCp or RMgOAr compound was added to a benzene-d_6 solution of the macrocycle. The amounts used often corresponded to ca. 1 M concentrations of the components, although spectra of less concentrated solutions were generally similar.

Preparation of RMg(macrocycle)$^+$Fl$^-$ and RMg(macrocycle)$^+$In$^-$. In a typical preparation, the macrocycle (1.0 mmol) was added to a solution of the R$_2$Mg compound (1.1 mmol) in diethyl ether (2 mL). As this solution was stirred, a solution of indene or fluorene (1.0 mmol) in diethyl ether (1 mL) was added over ca. 1 min, and then the reaction was then allowed to proceed overnight. Products of the fluorene preparations were orange precipitates, and those of the indene preparations were blue-green precipitates. A precipitate was filtered from the solution and washed with diethyl ether; the ether then was allowed to evaporate.

Supporting Information Available: Text and a table giving further results of *i*-BuMgCp−15C5 experiments; purification of reagents; syntheses of R$_2$Mg compounds; preparations of RMgCp and RMgOAr compounds; NMR spectra of RMgCp−macrocycle and RMgOAr−macrocycle preparations; NMR spectra of RMg(macrocycle)$^+$Fl$^-$ and RMg(macrocycle)$^+$In$^-$ solutions; details of the X-ray structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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