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Reactions of Grignard Reagents with an Azacrown Ether: Syntheses of $RMg(14N4)^+RMgX_2^-$ and $RMg(14N4)^+X^-$

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In the presence of some macrocyclic compounds, diorganomagnesium compounds disproportionate to magnesiate anions and coordinated organomagnesium cations.[1-3] With a favorable cryptand (2,1,1-cryptand)[1] or azacrown ether (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane = 14N4)[3] and benzene as the solvent, conversion of dialkyl- and diarylmagnesium compounds to the coordinated cation and magnesiate anion shown in eq 1[4] (C = a macrocyclic compound) can be essentially

$$2R_2Mg + C \rightarrow RMgC^+ + R_3Mg^- \qquad (1)$$

quantitative. Magnesiate ions are more reactive than ordinary organomagnesium compounds (R_2Mg, RMgX) and in some reactions give substantially different product compositions.

Interaction with macrocyclic compounds of a Grignard reagent (RMgX) instead of a diorganomagnesium compound (R_2Mg) would be interesting and potentially more useful. If the reaction in eq 2 occurs, then the anion would be a benign halide rather than a reactive magnesiate, whose presence complicates efforts to study features of $RMgC^+$ cations. If the reaction in eq 3

$$RMgX + C \rightarrow RMgC^+ + X^- \qquad (2)$$

$$2RMgX + C \rightarrow RMgC^+ + RMgX_2^- \qquad (3)$$

occurs, then a new magnesiate ion composition[5] would be produced. Since it is prepared directly from an organic halide, a Grignard reagent also is a more desirable reactant than is R_2Mg.[6]

Addition of a macrocyclic compound to diethyl ether or THF solutions of Grignard reagents seems an obvious way to prepare solutions having the ions indicated in eqs 2 and 3. Such additions to Grignard reagent solutions having sufficient concentrations ($\geq$0.1 M) to be conveniently studied by routine NMR spectroscopy, however, generally have produced large amounts of solid.[7] In instances where this behavior has been examined, the halide is in the solid and some R_2Mg remains in solution. We now have found a procedure, however, that in many cases prepares *solutions* of ions from Grignard reagents and a macrocyclic compound.

A THF solution of a Grignard reagent is prepared in the usual fashion, and solvent is removed using reduced pressure and heat (typically <0.1 Torr, 60–90 °C, 12–24 h). Titration of base and halide in the solids or oils that remain indicates most to have R-to-X ratios of 0.95–1.00. Most of these materials are very soluble in benzene; ^1H NMR spectra of the solutions show 1–2 THFs per R.[8] Examples of solids are *i*-PrMgCl$(THF)_{1.0}$ (mp 42–50 °C), *i*-BuMgBr$(THF)_{1.0}$, (*p-tert*-butylphenyl)MgBr$(THF)_{1.2}$ (mp 70–80 °C), and (*p*-methylphenyl)MgI$(THF)_{1.0}$; examples of oils are $(CH_3CH_2)_2CHCH_2MgBr(THF)_{1.0}$[9] and *i*-BuMgI$(THF)_{1.2}$.[9]

^1H NMR spectra of benzene-d_6 solutions prepared from *i*-BuMgI(THF) (an amount that would give a 0.4 M solution) and 14N4 are shown in Figure 1. The upper spectrum is of a solution prepared using an *i*-BuMgI-to-14N4 ratio of ~2.0. Two equal sets of isobutyl absorptions are seen. The set labeled A (CH_2 at δ –0.78, CH_3 at δ 1.12, CH partially obscured at δ ~1.75) has positions similar to those seen[3] for *i*-BuMg$(14N4)^+$ with other anions (e.g., fluorenide). Moreover, most 14N4 absorptions are similar to those[3] of other $RMg(14N4)^+$ cations. The set of isobutyl aborptions labeled B (CH_2 at δ 0.18, CH_3 at δ 1.46, CH at δ 2.58) must be due to *i*-BuMgX_2.[5] The lower spectrum is of a solution resulting from a preparation that used an *i*-BuMgI-to-14N4 ratio of ~1.0. Some precipitation occurred, but the concentration of isobutyl groups is ~0.2 M at ambient temperature. Since this spectrum shows the absorptions attributed to *i*-BuMg$(14N4)^+$ *but no other absorptions*, the anion must be I^-. One prominent absorption (labeled C) of four Hs of 14N4 has significantly different positions in the two spectra: δ 3.38 when the anion is $RMgI_2^-$, δ 4.39 when it is I^-. The position of this absorption has also varied markedly with the anion in other cases; for example, it is δ 2.34 when the anion accompanying *i*-BuMg$(14N4)^+$ is $(i\text{-Bu})_3Mg^-$ and δ 4.58 when the anion is Br^-. We assign this absorption to Hs (NCH*H*CH_2CH*H*N) of the 3-carbon bridges that are on the side of the ring opposite R.[10]

Benzene solutions of $RMg(14N4)^+RMgX_2^-$ also result from 2:1 ratios of 14N4 and other RMgX(THF) species in which R is alkyl or aryl and X is Br or I. Examples include preparations from EtMgBr, *t*-BuMgBr, (*p-tert*-butylphenyl)MgBr, *i*-PrMgI, and (*p*-methylphenyl)MgI. When a 1:1 ratio of reactants is used, however, precipitates form, which presumably are $RMg(14N4)^+X^-$. Besides *i*-BuMg$(14N4)^+I^-$, a few others are somewhat soluble: $(CH_3CH_2)CHCH_2Mg(14N4)^+Br^-$, for example, dissolves to the extent of about 0.15 M at ambient temperature, and $EtMg(14N4)^+I^-$ dissolves sufficiently to give a reasonable ^1H NMR spectrum.

When X is Cl, RMgX and 14N4 in 2:1 ratio provide benzene solutions that exhibit ^1H NMR absorptions for $RMg(14N4)^+$ and $ClMg(14N4)^+$. With *i*-PrMgCl, for example, two of the characteristic low-field 14N4 absorptions are seen. One (δ 3.79) and a matching set of *i*-Pr absorptions can be assigned to *i*-PrMg$(14N4)^+$. The other (δ 4.06), of somewhat less intensity, lacks an accompanying set of isopropyl absorptions and must be due to $ClMg(14N4)^+$. The reactions in eqs 4 and 5 both are

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[1] Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985,** *107,* 432. Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987,** *109,* 2510. Kushlan, D. M., The Pennsylvania State University, unpublished observations.

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

[3] Pajerski, A. D., unpublished observations and Ph.D. dissertation, The Pennsylvania State University, 1990.

[4] Although formulas such as R_3Mg^- and $RMgX_2^-$ are written for magnesiate ions, it is possible that the species in solution include dianions that are dimers of these formulas.

[5] A solution in which the anion has the average composition $RMgX_2^-$ also may contain MgX_3^-, R_2MgX^-, and R_3Mg^-, since these anions would equilibrate.

[6] For reviews of preparations and properties of organomagnesium compounds, see: Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 4. Nützel, K. *Methoden Org. Chem.* (*Houben-Weyl*), *4th Ed.* **1973,** *13*(2a), 47.

[7] There is a report that crown ethers and alkylmagnesium halides at low concentrations (~10^{-4} M) give homogeneous solutions [Bogatskii, A. V.; Chumachenko, T. K.; Luk'yanenko, N. G.; Lyamtseva, L. N.; Starovoit, I. A. *Dokl. Chem.* (*Engl. Transl.*) **1980,** *251,* 105; *Dokl. Akad. Nauk SSSR* **1980,** *251,* 113].

[8] Solutions that must be similar have been prepared by reactions of organic halides and Mg in aromatic hydrocarbon solvents containing 1 THF per Mg [for example: Leigh, T. *Chem. Ind.* (*London*) **1965,** 426. Canonne, P.; Foscolos, G.; Caron, H.; Lemay, G., *Tetrahedron* **1982,** *38,* 3563].

[9] A solid of composition $RMgX(THF)_2$ remains after THF is removed at reduced pressure and ambient temperature. This oil results, however, when the solid is heated at ~90 °C at reduced pressure.

[10] Crystal structures of $RMg(14N4)^+$ cations show R and the 14N4 methyls to be on the same side of the 14N4 ring.[3] The four Hs referred to are on the other side of the ring and approximately perpendicular to its average plane; they look particularly vulnerable to interactions with the anion.

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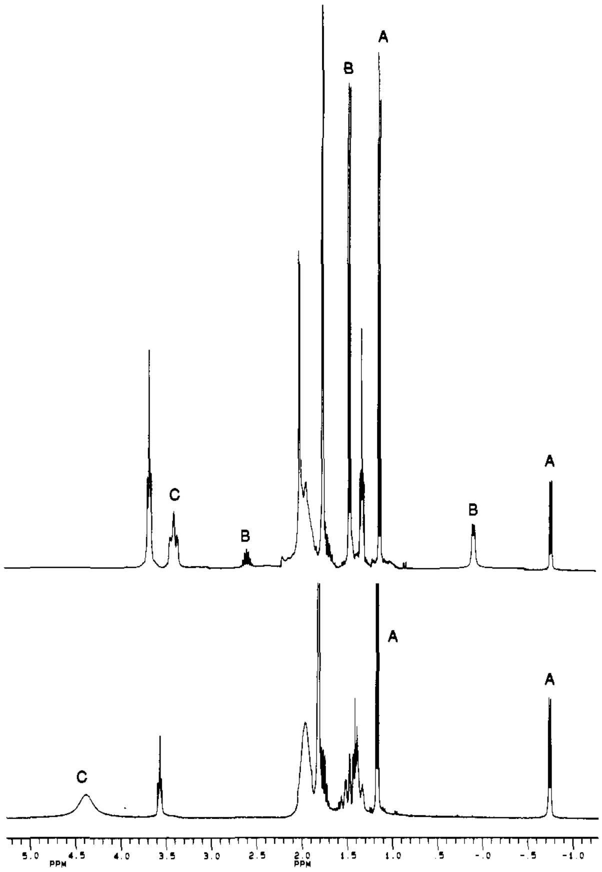

Figure 1. ^{1}H NMR spectra (300 MHz) of benzene-d_6 solutions of *i*-BuMg(14N4)$^+$*i*-BuMgI$_2^-$ (upper spectrum, concentration ~0.2 M) and *i*-BuMg(14N4)$^+$I$^-$ (lower spectrum, concentration ~0.2 M); chemical shifts are relative to benzene-d_5 (δ 7.15). Isobutyl absorptions of *i*-BuMg(14N4)$^+$ are labeled A, and those of *i*-BuMgI$_2^-$ are labeled B. An absorption assigned to a group of 4Hs (NCH*H*CH$_2$CH*H*N) of a coordinated 14N4 is labeled C and discussed in the text. THF freed from the *i*-BuMgI(THF) used in the preparations contributes absorptions at δ 1.3–1.4 and 3.6–3.7.

significant.[11] That only one set of R absorptions is seen for the anions is expected since Rs in species such as RMgCl$_2^-$ and

$$2\text{RMgCl} + 14\text{N4} \rightarrow \text{RMg(14N4)}^+ + \text{RMgCl}_2^- \quad (4)$$

$$2\text{RMgCl} + 14\text{N4} \rightarrow \text{ClMg(14N4)}^+ + \text{R}_2\text{MgCl}^- \quad (5)$$

R$_2$MgCl$^-$ should exchange rapidly. In accord with the stoichiometry (eqs 4 and 5), the R absorptions of the anion are stronger than those of RMg(14N4)$^+$. Except for additional absorptions due to free 14N4, the spectrum is similar when the *i*-PrMgCl-to-14N4 ratio is 2:1 instead of 1:1. Therefore, substantial ionization to *i*-PrMg(14N4)$^+$Cl$^-$ is not taking place.[12] It is not surprising that the smaller Cl is more difficult than Br or I to dislodge from Mg.

Within the limits of routine NMR observations, RMg(14N4)$^+$ is the only cation when X = Br or I but is accompanied by a significant amount of XMg(14N4)$^+$ when X = Cl. The equilibrium in eq 6, therefore, lies considerably more to the left for Cl than for Br or I. Because of its positive charge, however,

$$\text{XMg(14N4)}^+ + \text{R}_2\text{MgX}^- \rightleftarrows \text{RMg(14N4)}^+ + \text{RMgX}_2^- \quad (6)$$

XMgC$^+$ might be expected to be formed more with Br and I than with the more electronegative Cl. Similarly, absorptions of α-Hs of R of RMgC$^+$ (C = a macrocyclic compound) might be expected to be downfield rather than strikingly *upfield*. Perhaps the large number of groups strongly bonded and contributing electrons to Mg in such cations (e.g., five bonds in RMg(14N4)$^+$, seven in RMg(2,1,1-cryptand)$^+$) greatly reduces its electropositive character. Other factors, of course, could contribute to the preferential formation of ClMg(14N4)$^+$, for example, an adverse steric interaction between X and 14N4 in XMg(14N4)$^+$, which is smallest when X = Cl.

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(11) This is analogous to the formation of both R$_2$Al(crown)$^+$ and RAlX(crown)$^+$ from R$_2$AlX and crown ethers [Richey, H. G., Jr.; BergStresser, G. L. *Organometallics* **1988**, *7*, 1459].

(12) If the system is completely described by eqs 4 and 5, then (R in anions)/(R in cation) = (2 – Z)/Z where Z is [RMg(14N4)$^+$]/{[RMg(14N4)$^+$] + [ClMg(14N4)$^+$]}. In fact, the ratio of areas of ^{1}H NMR absorptions of R in anions to those of R in a cation is generally somewhat less than expected on this basis. The deviation, however, is not outside our estimate of uncertainties that could alter the ratio, including errors in measuring the Cl:R ratio in the RMgCl preparation, errors in integrating areas of NMR absorptions, and the inability to detect or define small amounts of materials that may separate from solutions.