

the catalyst by two trap-to-trap distillations (recovery ca. 100%) and analyzed by GLC (column D). Quantitative estimation of the composition of the reaction mixture from the ampule heated at 97.5 °C is accomplished by "cut and weigh" of enlarged traces from 10 copies of the chromatogram ( $K = 1.1 \pm 0.1$ ).

**Acknowledgment.** Grateful appreciation is expressed by D.W.A. for support under a National Institutes of Health training grant to the Department of Chemistry, Harvard University, by L.B. to

the late John and Elizabeth Bates Cowles for the award of a fellowship, and by M.P. to the Norman Fund in Organic Chemistry for fellowship support. We express our thanks to Dr. Eric T. Fossel for determining the LIS.

**Registry No.** 2, 93756-93-5; 3, 93756-94-6; 4, 30708-54-4; 4 (tosyl-hydrazone), 93756-96-8; RuH(NO)(PPh<sub>3</sub>)<sub>3</sub>, 33991-11-6; 3-quinuclidone, 3731-38-2; 3-quinuclidone-2,2-d<sub>2</sub>, 34291-53-7; 1-azabicyclo[3.2.2]nonan-4-one-2,2-d<sub>2</sub>, 93756-95-7; 3-quinuclidone hydrochloride, 1193-65-3.

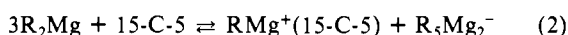
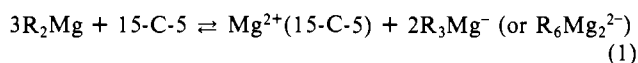
## Magnesiate Ions in Solutions and Solids Prepared from Dialkylmagnesium Compounds and Cryptands

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**Abstract:** Addition of 2,1,1-cryptand to diethylmagnesium solutions greatly speeds reactions with pyridine and leads to formation of significant amounts of a 1,4- as well as a 1,2-addition product, observations attributed to formation of magnesiate species. In crystalline [EtMg<sup>+</sup>(2,2,1-cryptand)]<sub>2</sub> Et<sub>6</sub>Mg<sub>2</sub><sup>2-</sup>, the magnesiums of the dianion are identical and have essentially a tetrahedral bonding geometry. They share two bridging ethyl groups, and each is bonded to two terminal ethyl groups. The magnesium of the cation is bonded to five of the heteroatoms of the cryptand and to the ethyl group. In crystalline NpMg<sup>+</sup>(2,1,1-cryptand) Np<sub>3</sub>Mg<sup>-</sup>, the magnesium of the anion has a trigonal planar bonding geometry. The coordination geometry of the magnesium of the cation is essentially that of a pentagonal bipyramid with bonds to all six of the heteroatoms of the cryptand and a bond to the neopentyl group. The <sup>1</sup>H NMR spectrum of a benzene solution of this solid is consistent with the presence of the same ions in the solution.

Earlier work on the consequences of adding 15-crown-5 to diethyl ether or tetrahydrofuran solutions of dialkylmagnesium compounds led to the proposal that striking chemical properties of the resulting solutions were due to low concentrations of magnesium "ate" species, such as R<sub>3</sub>Mg<sup>-</sup>, formed by equilibria such as those in eq 1 and 2.<sup>2</sup> In this paper we report much stronger evidence for the formation of such anions.



It was reasonable that an appropriate cryptand might coordinate Mg<sup>2+</sup> or RMg<sup>+</sup> more effectively than does 15-crown-5, and models indicated 2,1,1-cryptand to be a particularly attractive possibility. The models were constructed<sup>3</sup> both (1) by considering magnesium to be an ion (Mg<sup>2+</sup>) with a radius of 0.7–0.8 Å and the atoms bonded to it to have conventional van der Waals radii and (2) by considering magnesium to be covalently bonded and the Mg–C, Mg–N, and Mg–O bonds to have typical lengths observed in crystal structures. Models of both sorts indicated that all heteroatoms of the cryptand could potentially bond to magnesium, enveloping it so effectively that no more than one bond to any other group would be possible.

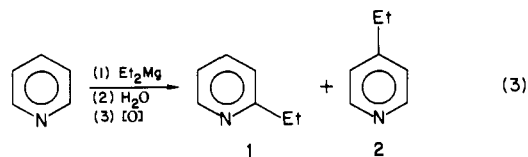
Addition of 2,1,1-cryptand to diethyl ether solutions of Et<sub>2</sub>Mg resulted in immediate formation of precipitates. Such suspensions exhibited reactivity toward added pyridine similar to that of solutions<sup>2</sup> formed by adding 15-crown-5 to Et<sub>2</sub>Mg. In the absence of an additive, addition of Et<sub>2</sub>Mg is very slow and produces exclusively **1**. Addition of 15-crown-5 leads to much more rapid additions that also produce significant amounts of **2**. As indicated by the results summarized in Table I, even relatively small amounts

**Table I.** Product Compositions from Reactions of Diethylmagnesium, Cryptands, and Pyridine in Diethyl Ether at 25 °C<sup>a</sup>

relative molar amounts <sup>b</sup>			additive	1, <sup>c</sup> %	2, <sup>c</sup> %
Et <sub>2</sub> Mg	cryptand	pyridine			
1	0	2		0.6	<0.01
1	0.03	1.5	2,1,1-cryptand	2	8
1	0.05	2	2,1,1-cryptand	6	12
1	0.2	0.75	2,1,1-cryptand	4	22
1	1	0.5	2,1,1-cryptand	13	24
1	1	1	2,1,1-cryptand	14	31
1	1	2	2,1,1-cryptand	15	15
3	1	1	2,1,1-cryptand	10	24
1	0.05	1	2,2,1-cryptand	0.5	2
1	1	2	2,2,1-cryptand	15	10
2	1	1	2,2,1-cryptand	20	25
3	1	1	2,2,1-cryptand	10	28
1	1	1	2,2,2-cryptand	5	2
2	1	1	2,2,2-cryptand	4	10

<sup>a</sup> Reaction times are ~24 h. <sup>b</sup> The concentration of pyridine generally was ~0.1 M. <sup>c</sup> Yields are based on mol of **1** and **2** per mol of Et<sub>2</sub>Mg or pyridine, whichever was in lesser amount.

of 2,1,1-cryptand produced the same effects.<sup>4</sup> Suspensions formed by adding 2,2,1-cryptand or 2,2,2-cryptand to Et<sub>2</sub>Mg showed similar reactivity.



We have not succeeded in obtaining crystals suitable for single-crystal X-ray analysis from solids prepared from Et<sub>2</sub>Mg and

(1) Most of this material is taken from: Squiller, E. P. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1984.

(2) Richey, H. G., Jr.; King, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 4672.

(3) The cryptand was constructed by using CPK space-filling molecular models (Ealing Corp.).

(4) The yields of **1** and **2** do not increase greatly with longer reaction times. Metalation of pyridine, a significant competing reaction, is at least one limitation to these yields.

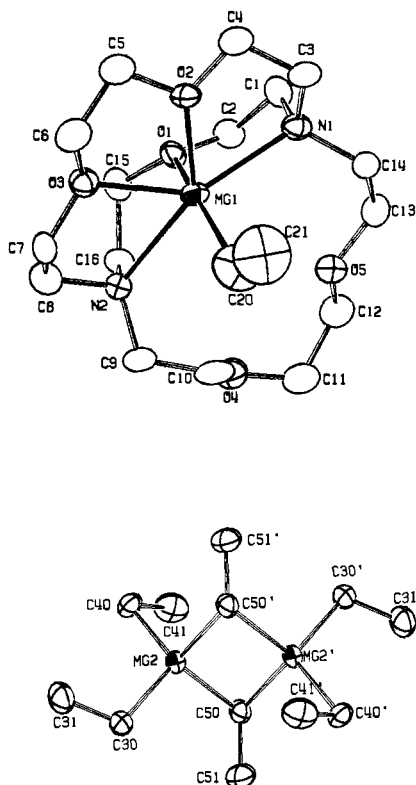


Figure 1. ORTEP drawings of  $\text{EtMg}^+(2,2,1\text{-cryptand})$  and  $\text{Et}_6\text{Mg}_2^{2-}$ . Atoms are shown with 20% probability ellipsoids. The closest approach between the magnesium of a cation and a magnesium of an anion is 7.33 Å; the closest approach of a magnesium of an anion to a heteroatom of a cryptand is 5.22 Å.

2,1,1-cryptand but we have from  $\text{Et}_2\text{Mg}$  and 2,2,1-cryptand. Addition of a solution of 2,2,1-cryptand (5 mg, 0.015 mmol) in tetrahydrofuran (1 mL) to a tetrahydrofuran–diethyl ether (1:1) solution of  $\text{Et}_2\text{Mg}$  (2.0 mL, 0.22 M, 0.45 mmol) did not lead to formation of a solid. When an equal volume of pentane was layered onto this solution and it was allowed to stand for 24 h, however, crystals formed that were suitable for X-ray analysis.

Analysis<sup>5,6</sup> (refined to  $R = 0.089$  and  $R_w = 0.103$ ) of one of the crystals showed it to contain a 2:1 ratio of species with the compositions  $\text{EtMg}^+(2,2,1\text{-cryptand})$  and  $\text{Et}_6\text{Mg}_2^{2-}$  and presumably with the indicated charges. ORTEP drawings of the ions are shown in Figure 1. The magnesiums in the dianion, equivalent by symmetry, have essentially a tetrahedral bonding geometry. The ring bond angle at magnesium ( $\text{C}(50)\text{-Mg}(2)\text{-C}(50')$ ) is  $106.8(3)^\circ$  and the external bond angle ( $\text{C}(30)\text{-Mg}(2)\text{-C}(40)$ ) is  $114.4(4)^\circ$ .<sup>7</sup> The ring bond angle at carbon ( $\text{Mg}(2)\text{-C}(50)\text{-Mg}(2')$ ) is  $73.2(3)^\circ$ . In the dianion, the Mg–Mg distance is 2.816(5) Å and the other bond lengths at magnesium are  $\text{Mg}(2)\text{-C}(30) = 2.238(9)$  Å,  $\text{Mg}(2)\text{-C}(40) = 2.209(9)$  Å, and  $\text{Mg}(2)\text{-C}(50)$  and  $\text{Mg}(2)\text{-C}(50') = 2.359(9)$  and  $2.364(9)$  Å. The magnesium of the cation is bonded to five heteroatoms of the cryptand but remote from the two oxygens of one of the longer cryptand bridges.

A species that formally is  $(\text{Li})_2\text{Ph}_6\text{Mg}_2^{2-}$  has been prepared, but the crystal structure shows strong Mg–Ph–Li bridge bonding ( $\text{LiPh}_2\text{MgPh}_2\text{MgPh}_2\text{Li}$ , each lithium also bonded to the two N's

(5) Intensity data were collected on an Enraf-Nonius CAD-4 automatic diffractometer by using  $\text{Mo K}_\alpha$  radiation and the  $\theta$ - $2\theta$  scan technique. All calculations were performed on a Digital Equipment Corp. PDP 11/34 computer by using the Enraf-Nonius SDP Plus program library, version 1.0.

(6) Crystal data for  $[\text{EtMg}^+(2,2,1\text{-cryptand})]_2 \text{Et}_6\text{Mg}_2^{2-}$ ,  $\text{C}_{48}\text{H}_{104}\text{Mg}_4\text{N}_2\text{O}_{10}$ :  $a = 10.514(2)$  Å,  $b = 8.560(4)$  Å,  $c = 32.250(10)$  Å,  $\beta = 90.34(2)^\circ$ ;  $V = 2903(3)$  Å<sup>3</sup>; space group  $P2_1/n$ , no. 14;  $Z = 2$ ;  $D(\text{calcd}) = 1.138$  g cm<sup>-3</sup>. Of the 2910 unique reflections that were measured, 1422 were observed ( $I > 2\sigma(I)$ ). The structure was solved by direct methods (MULTAN 78).

(7) Numbers in parentheses are estimated standard deviations in the least significant digit.

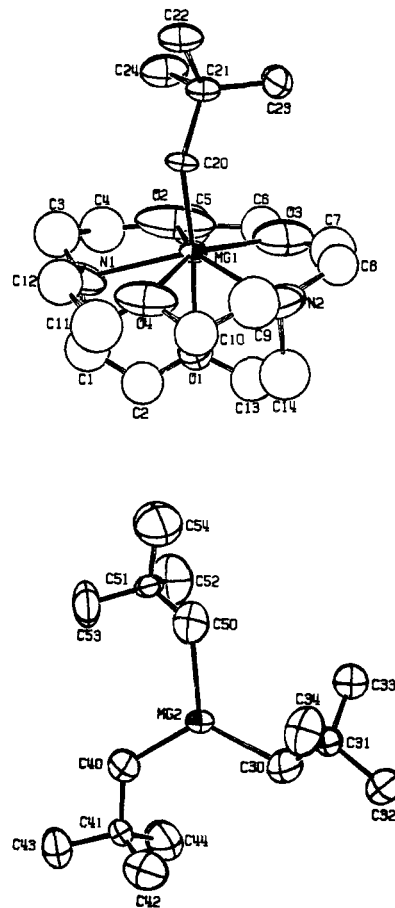


Figure 2. ORTEP drawings of  $\text{NpMg}^+(2,1,1\text{-cryptand})$  and  $\text{Np}_3\text{Mg}^-$ . Atoms are shown with 20% probability thermal ellipsoids. The closest approach between the magnesium of a cation and that of an anion is 7.18 Å; the closest approach of the magnesium of an anion to a heteroatom of a cryptand is 5.71 Å.

of a  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ ).<sup>8</sup> The ring angles of  $106.8(3)^\circ$  and  $73.2(3)^\circ$  and the Mg–Mg distance of 2.816(5) Å in  $\text{Et}_6\text{Mg}_2^{2-}$  are relatively similar, however, to the angles of  $102.7(1)^\circ$  and  $77.3(3)^\circ$  and the Mg–Mg distance of 2.882(2) Å of the hexaphenyl compound.  $\text{Et}_6\text{Mg}_2^{2-}$  is in a sense a fragment lifted out of the linear polymeric structure of pure  $\text{Et}_2\text{Mg}$ . The angles for the dianion are close to those ( $108^\circ$  and  $72^\circ$ ) determined<sup>9</sup> for the polymer, though the Mg–Mg distance in the dianion is longer than that in the polymer (2.67(1) Å). The ring bond angles of  $\text{Et}_6\text{Mg}_2^{2-}$  also are similar to those ( $105.3(4)^\circ$  and  $74.7(4)^\circ$ )<sup>10</sup> of the isoelectronic  $\text{Me}_6\text{Al}_2$  though the Mg–Mg distance is decidedly longer than the Al–Al distance (2.600(4) Å).

A crystalline solid precipitated about 30 min after addition of a solution of 2,1,1-cryptand (100 mg, 0.35 mmol) in diethyl ether (~3 mL) to a solution of  $\text{Np}_2\text{Mg}$  (58 mg, 0.35 mmol) (Np = neopentyl) in diethyl ether (5 mL). Crystals suitable for single-crystal X-ray analysis were obtained by dissolving this solid in tetrahydrofuran (~6 mL), layering an equal volume of pentane over the solution, and waiting 24 h.

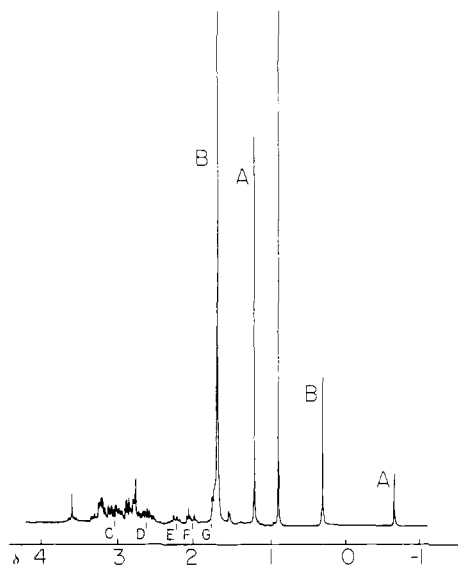
Although relatively high discrepancy indices ( $R = 0.132$ ,  $R_w = 0.157$ ) were obtained in the final refinement of the single-crystal X-ray analysis,<sup>5,11</sup> the results were more than adequate to clearly

(8) Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3726.

(9) Weiss, E. *J. Organomet. Chem.* **1965**, *4*, 101. For dimethylmagnesium, the ring bond angles are  $105(2)^\circ$  and  $75(2)^\circ$  and the Mg–Mg distance is 2.72(2) Å [Weiss, E. *J. Organomet. Chem.* **1964**, *2*, 314].

(10) Vranka, R. G.; Amma, E. L. *J. Am. Chem. Soc.* **1967**, *89*, 3121.

(11) Crystal data for  $\text{NpMg}^+(2,1,1\text{-cryptand}) \text{Np}_3\text{Mg}^-$ ,  $\text{C}_{34}\text{H}_{72}\text{Mg}_2\text{N}_2\text{O}_4$ :  $a = 13.219(4)$  Å,  $b = 14.740(6)$  Å,  $c = 21.315(9)$  Å,  $\beta = 104.41(3)^\circ$ ;  $V = 4022(5)$  Å<sup>3</sup>; space group  $P2_1/c$ , no. 14;  $Z = 4$ ;  $D(\text{calcd}) = 1.026$  g cm<sup>-3</sup>. Of the 4726 unique reflections that were measured, 1516 were observed ( $I > 3\sigma(I)$ ). The structure was solved by direct methods (MULTAN 78).



**Figure 3.** The 200-MHz  $^1\text{H}$  NMR spectrum in  $\text{C}_6\text{D}_6$  of the solid formed from 2,1,1-cryptand and  $\text{Np}_2\text{Mg}$ . Chemical shifts are relative to benzene ( $\delta$  7.15). The absorptions labeled A are assigned to  $\text{NpMg}^+(\text{cryptand})$  and those labeled B to  $\text{Np}_3\text{Mg}^-$ . The absorption at 0.90 is due to neopentane.

show the structure. The crystal contains species with the compositions  $\text{NpMg}^+(2,1,1\text{-cryptand})$  and  $\text{Np}_3\text{Mg}^-$  and presumably with the indicated charges. ORTEP drawings of these ions are shown in Figure 2. The magnesium of the anion has essentially a planar trigonal bonding geometry. The three C–Mg–C bond angles are 116.9 (5), 117.6 (5), and 124.8 (5) $^\circ$ , and the Mg–C bond lengths are 2.125 (12), 2.240 (12), and 2.296 (16) Å. The magnesium of the cation has essentially a pentagonal bipyramidal bonding geometry. As had been anticipated from the examination of models, all six heteroatoms of the cryptand are bonded to the magnesium, five of the heteroatoms and the magnesium lying approximately in a plane. The oxygen of one of the short bridges of the cryptand and the neopentyl group occupy the apical sites.

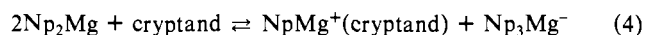
We know of no structures of magnesium-containing species related closely to the  $\text{Np}_3\text{Mg}^-$  ion reported here. In fact, except for a rare zeolite with a deeply buried magnesium that may be trivalent,<sup>12</sup> there seems to be no crystal structure of a trivalent magnesium compound.<sup>13</sup> The  $\text{Np}_3\text{Mg}^-$  ion is isoelectronic with trialkylaluminum monomers, and its geometry is close to the planar trigonal geometry inferred for gaseous  $\text{Me}_3\text{Al}$  by an electron diffraction study,<sup>14</sup> although the average Mg–C bond length (2.22 Å) is considerably longer than the Al–C bond length (1.964 (3) Å). The Mg–C bond length in  $\text{Np}_3\text{Mg}^-$  is also longer than that in gaseous  $\text{Np}_2\text{Mg}$  (2.126 (6) Å).<sup>15</sup> The pentagonal bipyramidal geometry found in the cation apparently can be favorable for magnesium. It is also found in the crystal structure<sup>16</sup> of  $\text{Mg}(\text{S-CN})_2$  coordinated to benzo-15-crown-5 (the SCN's occupying the apical positions) and in some structures<sup>17</sup> involving noncyclic ligands.

Do the ions seen in the crystal structures also exist in a significant concentrations in solution? Limited solubility and other problems have made it difficult to obtain satisfactory NMR spectra

of solutions of such solids. The greatest success has been with a solid that was obtained by adding 2,1,1-cryptand to a diethyl ether solution of  $\text{Np}_2\text{Mg}$  and that proves to be more soluble in benzene than in diethyl ether. A  $^1\text{H}$  NMR spectrum (Figure 3) of a  $\text{C}_6\text{D}_6$  solution of this solid shows absorptions that can be assigned to a cryptand ( $\delta$  1.5–3.6) and to neopentyl groups in two environments (A,  $\delta$  –0.62 for the  $\text{CH}_2$  and  $\delta$  1.20 for the  $\text{CH}_3$ 's; B,  $\delta$  0.27 for the  $\text{CH}_2$  and  $\delta$  1.64 for the  $\text{CH}_3$ 's). The absorptions due to the cryptand are much more complex than those exhibited by the cryptand alone, indicating a greater number of environments for its hydrogens. Moreover, absorptions of some hydrogens are shifted upfield by at least 1.0 ppm. The absorption areas indicate that the relative amounts are 1:1:3 cryptand:Np(A):Np(B).

Upon addition of cryptand to the NMR sample, the spectrum in Figure 3 is unchanged except for the appearance of new absorptions identical with those exhibited by the cryptand alone. Therefore, exchange between cryptand already present and added cryptand is slow on the NMR time scale. Upon addition of  $\text{Np}_2\text{Mg}$  to the original NMR solution, the absorptions due to the single neopentyl group (A) and to the cryptand are unchanged, but common  $\text{CH}_2$  and  $\text{CH}_3$  absorptions are observed for the group of three neopentyls (B) and for the neopentyls of the added  $\text{Np}_2\text{Mg}$ .

The NMR spectrum and the effects of added cryptand and  $\text{Np}_2\text{Mg}$  are particularly compatible with a proposal that the equilibrium shown in eq 4 lies to the right in benzene, the dominant



species in solution being the  $\text{NpMg}^+$  (cryptand) and  $\text{Np}_3\text{Mg}^-$  ions present in the crystal.<sup>18</sup> If the magnesium of  $\text{NpMg}^+$  is in the cryptand cavity, then it should have no accessible coordination site to facilitate exchange of its Np with those of  $\text{Np}_3\text{Mg}^-$  or added  $\text{Np}_2\text{Mg}$ , and such exchange could be slow. Exchange with external cryptand would require breaking all Mg–O and Mg–N bonds and should be particularly slow. Exchange of the Np's of the anion with external  $\text{Np}_2\text{Mg}$  via equilibria such as that in eq 5 could reasonably be rapid. Of course, the NMR spectrum also is



consistent with the presence of  $\text{Np}_6\text{Mg}_2^{2-}$ , an ion analogous to the  $\text{Et}_6\text{Mg}_2^{2-}$  seen in the other crystal structure, if the terminal and bridging neopentyl groups exchange rapidly with each other and with those of any  $\text{Np}_3\text{Mg}^-$  present. Such exchange could occur readily by dissociation and recombination ( $\text{Np}_6\text{Mg}_2^{2-} \rightleftharpoons 2\text{Np}_3\text{Mg}^-$ ).

The most successful  $^1\text{H}$  NMR spectra involving ethyl groups have been obtained of solutions prepared by adding 2,1,1-cryptand or 2,2,1-cryptand to benzene suspensions of  $\text{Et}_2\text{Mg}$ . In solutions obtained so far, the ratio of ethyl groups to cryptand units (at least 6) has exceeded the alkyl to cryptand ratio (4) of the neopentyl solid described above. The spectra show two sets of ethyl absorptions. The absorptions of one set are sharp and invariant in position (in the 2,1,1-cryptand spectra, for example, a quartet at  $\delta$  –0.81 for the  $\text{CH}_2$  and triplet at  $\delta$  1.46 for the  $\text{CH}_3$ ). These absorptions and all cryptand absorptions ( $\delta$  1.6–3.3 for the 2,1,1-cryptand) can be assigned to  $\text{EtMg}^+(\text{cryptand})$ . The broader and more complex  $\text{CH}_2$  and  $\text{CH}_3$  absorptions of the other ethyl set (approximately  $\delta$  0.2 and 1.9) presumably are due to the ethyl groups of some mixture of neutral and anionic species such as  $\text{Et}_2\text{Mg}$ ,  $\text{Et}_3\text{Mg}^-$ ,  $\text{Et}_5\text{Mg}_2^{2-}$ , etc.<sup>19</sup>

(18) Results obtained from nuclear Overhauser difference spectroscopy, although not definitive, are consistent with this proposal. The regions labeled C–G in the spectrum were selectively irradiated (360 MHz). Irradiation at D enhanced (2.6%) the  $\text{CH}_2$ (A) absorption indicating that this neopentyl  $\text{CH}_2$  is in close proximity to a portion of the cryptand. The  $\text{CH}_2$ (B) absorption, due to the group of three neopentyls, was enhanced only by irradiation at G, and that could have been due to the proximity of G to the  $\text{CH}_3$ (B) absorption.

(12) Mortier, W. J.; Pluth, J. J.; Smith, J. V. *Nature (London)* **1975**, 256, 718.

(13) Structures containing trivalent magnesium have been proposed for a number of species in solution. For a review see: Pinkus, A. G. *Coord. Chem. Rev.* **1978**, 25, 173.

(14) Almenningen, A.; Halvorsen, S.; Haaland, A. *J. Chem. Soc., Chem. Commun.* **1969**, 644.

(15) Ashby, E. C.; Fernholt, L.; Haaland, A.; Seip, R.; Smith, R. S. *Acta Chem. Scand., Ser. A* **1980**, 34, 213.

(16) Owen, J. D. *J. Chem. Soc., Dalton Trans.* **1978**, 1418.

(17) For example, the coordination geometry of Mg in  $[\text{Mg}(\text{EDTA})\text{H}_2\text{O}]^{2-}$  in a crystal: Passer, E.; White, J. G.; Cheng, K. L. *Inorg. Chim. Acta* **1977**, 24, 13.

The observations reported here demonstrate the existence of solids containing magnesiate ions and strongly suggest that stable solutions containing significant concentrations of such ions can readily be formed.

(19) NMR observations indicated no significant interaction between  $\text{Et}_2\text{Mg}$  and 15-crown-5 in tetrahydrofuran but partial formation of 1:1 and 2:1 (which could perhaps have been 3:1) complexes in diethyl ether.<sup>2</sup> Particularly since  $^1\text{H}$  and  $^{13}\text{C}$  NMR absorptions of the ethyl groups underwent little change on addition of the crown ether, we assumed that "ate" species are formed only in small amounts and that the changes in chemical shifts observed in diethyl ether resulted from coordination of oxygens of the crown ether to intact  $\text{Et}_2\text{Mg}$ . Such coordination presumably was not significant in tetrahydrofuran because oxygens of 15-crown-5 could not compete effectively with those of tetrahydrofuran. We have now observed, however, that the  $^1\text{H}$  NMR spectra of some solutions formed by adding 15-crown-5 to a benzene solution of  $\text{Np}_2\text{Mg}$  show two sets of absorptions for the neopentyl groups consistent with the formation in the noncoordinating solvent of significant amounts of  $\text{NpMg}^+(\text{crown})$  and of magnesiate anions and leaves less certain the identity of the species responsible for the NMR shifts observed for diethyl ether solutions.

**Acknowledgment.** We are grateful to the National Science Foundation for support of this research and for aiding in the purchase of the NMR spectrometers. We thank Professor Lloyd Jackman for numerous helpful discussions and Alan Freyer for obtaining the high-field NMR spectra.

**Registry No.** 1, 100-71-0; 2, 536-75-4;  $[\text{EtMg}^+(2,2,1\text{-cryptand})]_2\text{Et}_2\text{Mg}_2^{2-}$ , 93842-25-2;  $\text{NpMg}^+(2,1,1\text{-cryptand})\text{Np}_3\text{Mg}^-$ , 93842-28-5;  $\text{Et}_2\text{Mg}$ , 557-18-6;  $\text{Np}_2\text{Mg}$ , 19978-31-5;  $\text{Mg}$ , 7439-95-4; 2,1,1-cryptand, 31250-06-3; 2,2,1-cryptand, 31364-42-8; 2,2,2-cryptand, 23978-09-8; pyridine, 110-86-1.

**Supplementary Material Available:** ORTEP drawings of the unit cell and tables of atomic coordinates, bond angles and bond lengths, anisotropic thermal parameters, root-mean-square amplitudes of thermal vibration, and observed and calculated structure factor amplitudes for both crystal structure (42 pages). Ordering information is given on any current masthead page.

## Photoinduced Cyclizations of Mono- and Dianions of *N*-Acyl-*o*-chloroanilines and *N*-Acyl-*o*-chlorobenzylamines as General Methods for the Synthesis of Oxindoles and 1,4-Dihydro-3(2*H*)-isoquinolinones<sup>1</sup>

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Contribution from the Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061. Received December 15, 1983

**Abstract:** Formation of the monoanions of a series of *N*-acyl-*N*-alkyl-*o*-chloroanilines by means of LDA in THF followed by irradiation with near-UV light affords 1,3-dialkyloxindoles in good yields. Similar photoinduced cyclizations of dianions derived from *N*-acyl-*o*-chloroanilines leads to 3-alkyloxindoles. Photocyclizations of mono- and dianions prepared from  $\alpha,\beta$ -unsaturated *o*-haloanilides proceed to form 3-alkyldieneoxindoles. Carbanions derived from *N*-acyl-*o*-chlorobenzylamines also undergo photoassisted ring closure to afford 1,4-dihydro-3(2*H*)-isoquinolinones. The influence of near-UV light and the effect of inhibitors implicate a radical-chain mechanism as the major reaction pathway in this convenient new method for oxindole and isoquinolinone synthesis.

The importance of oxindoles and 1,4-dihydro-3(2*H*)-isoquinolinones as synthetic intermediates<sup>2</sup> and pharmaceutical agents<sup>3</sup> has led to development of numerous methods for their preparation.<sup>4</sup> Among these, considerable attention has been given

to reactions in which appropriate precursors having a side chain containing a reactive center positioned for construction of the heterocyclic ring are subjected to cyclization at the ortho position of an aromatic nucleus. For example, oxindoles are available by acid-catalyzed cyclization of  $\alpha$ -hydroxyacetanilides,<sup>5</sup> cyclization of *N*-(*o*-bromophenyl)acetamides in the presence of NaH and CuBr,<sup>6</sup> the traditional Lewis acid catalyzed cyclization of  $\alpha$ -haloacetanilides,<sup>7</sup> and by photocyclization of 2-(*N*-methylanilino)-acetoacetates followed by oxidative rearrangement.<sup>8</sup> 1,4-Dihydro-3(2*H*)-isoquinolinones have been synthesized by analogous intramolecular reactions, including acid-catalyzed cyclization of *N*-benzylamides derived from benzoic acid<sup>9</sup> and Friedel-Crafts cyclization of *N*-( $\alpha$ -chloroalkyl)phenylacetamides.<sup>10</sup> Recently,

(1) (a) Supported by National Science Foundation Grant CHE 80-22538. (b) From the Ph.D. dissertations of M. C. Sleevi, Virginia Polytechnic Institute and State University, June, 1979 and R. R. Goehring, Virginia Polytechnic Institute and State University, November, 1980. (c) For a preliminary report of this work, see: Wolfe, J. F.; Sleevi, M. C.; Goehring, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 3646. (d) Dedicated to Prof. Milos Hudlicky in honor of his 65th birthday.

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