Contribution from the School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia 30332

Preparation and Characterization of (Dialkylamino)- and (Diarylamino)magnesium Hydrides

E. C. ASHBY* and A. B. GOEL

Received August 30, 1977

A series of THF-soluble (dialkylamino)- and (diarylamino)magnesium hydrides, $HMgNR_2$ (where $NR_2 = NEt_2$, N(*n*-Pr)$_2$, N(*i*-Pr)$_2$, N(*n*-Bu)$_2$, N(*sec*-Bu)$_2$, NPh_2, N(Me)-*i*-Pr, 1-piperidinyl, 2,6-dimethyl-1-piperidinyl, and N(*t*-Bu)$SiMe_3$), has been synthesized by the reaction of active magnesium hydride with the corresponding bis(dialkylamino)- or bis(diarylamino)magnesium compounds in THF. These compounds were also prepared by the reaction of the appropriate amine with magnesium hydride. A third route for the preparation of the (dialkylamino)- and (diarylamino)magnesium hydrides involves reaction of the appropriate lithium dialkyl- or diarylamide with chloromagnesium hydride. These hydrides were characterized by elemental analysis, infrared, NMR and X-ray powder diffraction studies. Infrared absorption bands in the regions 1550–1630 and 600–700 cm^{-1} have been assigned to Mg–H stretching and bending modes, respectively, by comparison with the corresponding deuterated compounds. Molecular weight studies in refluxing THF (at 260 mmHg) have been carried out and probable structures of these compounds are discussed. These hydrides have been found to exhibit unusual stereoselectivity in their reduction of cyclic ketones.

Introduction

Wiberg and co-workers[1] in 1955 published a series of papers concerning the preparation of bis(dialkylamino)aluminum hydrides and bis(dialkylamino)boron hydrides. Sometime later Hawthorne and co-workers[2] reported the preparation of (dialkylamino)aluminum dihydrides. In 1968, Bell and Coates[3] reported the preparation of (dialkylamino)- and alkoxyberyllium hydrides as well as the preparation of *N*-(2-(dimethylamino)ethyl)-*N*-methylaminozinc hydride. Sometime ago we reported[4] the preparation of (dialkylamino)magnesium hydrides by the hydrogenation or metal hydride reduction of (dialkylamino)magnesium alkyls. Interest in the synthesis of (dialkylamino)magnesium hydrides has primarily involved the quest for soluble H–Mg compounds so that they could be evaluated as stereoselective reducing agents and also the desire to have a soluble H–Mg compound for infrared studies. Very recently, we were able to prepare a series of alkylmagnesium hydrides[5] and hydridomagnesium halides[6] and have shown that these compounds can function as the starting materials for the synthesis of complex metal hydrides.[6,7] These alkylmagnesium hydrides and hydridomagnesium halides were synthesized by the reaction of dialkylmagnesium compounds and magnesium halides with an active form of magnesium hydride in THF solvent (eq 1, 2). In order to generalize further this reaction route to HMgX compounds, reactions of magnesium hydride with bis(dialkylamino)magnesium compounds have been carried out in THF, and a series of (dialkylamino)- and (arylamino)magnesium hydrides has been synthesized.

$$R_2Mg + MgH_2 \xrightarrow{THF} 2RMgH \tag{1}$$

$$MgX_2 + MgH_2 \xrightarrow{THF} 2HMgX \tag{2}$$

Experimental Section

Apparatus. All reactions were carried out in an atmosphere of nitrogen either using a nitrogen-filled glovebox equipped with a special recirculating system[8] to remove oxygen (manganese oxide) and moisture (dry ice–acetone traps) or using Schlenk-tube techniques on a bench top.[9] Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer. Solution spectra were obtained in a cell with KBr windows and solid spectra were obtained as Nujol mulls using CsI plates. NMR spectra were recorded on a 60-MHz Varian spectrometer. X-ray powder diffraction data were obtained on a Philips-Norelco X-ray unit using a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 h. *d* spacings were evaluated using a precalibrated scale equipped with viewing apparatus. Line intensities were estimated visually. DTA–TGA data were obtained under vacuum using a modified Mettler Thermoanalyzer II.[10]

Analyses. Gas analyses were performed by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[9] Magnesium was determined by EDTA titration at pH 10 using Eriochrome Black T as an indicator.

Materials. Dialkylamines were dried over molecular sieve 4A and distilled prior to use. Diethyl ether was distilled immediately prior to use from $LiAlH_4$, and tetrahydrofuran was distilled from $NaAlH_4$. A solution of $LiAlH_4$ (Ventron, Metal Hydrides Division) was prepared by stirring a diethyl ether slurry overnight followed by filtration. The solution was standardized by aluminum analysis. Dimethyl- and diethylmagnesium in diethyl ether were prepared by the reaction of magnesium metal with dimethyl- and diethylmercury in the absence of solvent, followed by dissolution of the desired product in ether.[11]

A slurry of MgH_2 in THF was prepared by the reaction of diethylmagnesium with $LiAlH_4$ in diethyl ether followed by filtration and washing of the white solid with ether and finally preparation of the slurry by adding THF to the ether wet solid. Anal. Calcd for MgH_2: Mg:H = 1.00:2.00. Found: 1.00:2.02. Bis(dialkylamino)- and bis(diarylamino)magnesium compounds were prepared by reacting 2 equiv of amine with dimethylmagnesium in a mixture of diethyl ether and THF and refluxing the reaction mixture overnight. The solutions of bis(dialkylamino)- and bis(diarylamino)magnesium compounds were standardized by magnesium analysis. The absence of methane on hydrolysis of the samples was determined in order to establish the absence of CH_3–Mg bonds.

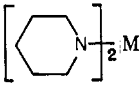
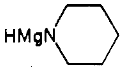
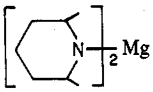
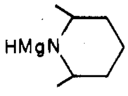
Preparation of *N*-(Trimethylsilyl)-*N*-*tert*-butylamine. To a well-stirred solution of *tert*-butylamine (50 mmol) in diethyl ether in the presence of triethylamine (50 mmol) was added dropwise trimethylchlorosilane. The reaction was highly exothermic and was cooled by an ice–water bath. An insoluble white solid of $Et_3N{\cdot}HCl$ formed and was filtered. The filtrate was concentrated by removing the diethyl ether solvent under vacuum and the product distilled at 117–125 °C. The infrared spectrum of the liquid product showed a strong band at 1250 cm^{-1} due to $\delta_s(CH_3)$ of MeSi and the presence of the Si–N bond was confirmed by the band at $\sim$770 cm^{-1}. The NMR spectrum of the product showed a singlet (due to Me_3Si protons) and also a singlet (due to *tert*-butyl protons) in 1:1 ratio.

Reaction of Bis(dialkylamino)- and Bis(diarylamino)magnesium Compounds with Magnesium Hydride Slurry in 1:1 Ratio in THF. To a well-stirred slurry of MgH_2 (5.00 mmol) in THF (25 mL) was added slowly bis(di-*n*-propylamino)magnesium (5.00 mmol) in 20 mL of THF. The reaction mixture was stirred at room temperature for $\sim$1 h to give a colorless clear solution. The product was analyzed (Table I) and its infrared spectrum recorded (Table II). The solvent was removed under vacuum to give a white solid. The X-ray powder diffraction pattern of the solid is reported in Table III.

Reaction of Dialkylamines with Magnesium Hydride in 1:1 Ratio in THF. The reaction of di-*n*-propylamine with MgH_2 will be used as a typical example for the preparation of bis(dialkylamino)magnesium hydrides from dialkylamines and MgH_2. Di-*n*-propylamine (0.54 g, 5.3 mmol) in THF (10 mL) was added dropwise to a MgH_2 (5.3 mmol) slurry in THF (30 mL) at −78 °C. The reaction mixture

0020-1669/78/1317-1862$01.00/0

Table I. Synthesis of $HMgNR_2$ Compounds by the Reaction of MgH_2 with $(R_2N)_2Mg$ Compounds in THF

No.	Reactants (mmol)		Reaction time, h	Solubility in THF	Nature of the product	Analysis Mg:(H or D)	Product
1	MgH_2 (4.5)	$(Et_2N)_2Mg$ (4.5)	20	Slightly soluble	Crystalline solid	1.00:0.95	$HMgNEt_2$
2	MgH_2 (5.0)	$(n\text{-}Pr_2N)_2Mg$ (5.0)	1	Moderately soluble	Foamy solid	1.00:0.98	$HMgN\text{-}n\text{-}Pr_2$
3	MgH_2 (4.0)	$(i\text{-}Pr_2N)_2Mg$ (4.0)	2	Moderately soluble	Crystalline solid	1.00:2.03	$HMgN\text{-}i\text{-}Pr_2$
4	MgH_2 (4.6)	$(n\text{-}Bu_2N)_2Mg$ (4.6)	3	Highly soluble	Foamy solid	1.00:0.97	$HMgN\text{-}n\text{-}Bu_2$
5	MgH_2 (5.3)	$(sec\text{-}Bu_2N)_2Mg$ (5.3)	3	Soluble, crystallized from THF	Crystalline solid	1.00:0.97	$HMgN\text{-}sec\text{-}Bu_2$
6	MgH_2 (5.25)	$(Ph_2N)_2Mg$ (5.25)	1	Soluble	Crystalline solid crystallized from THF	1.00:0.98	$HMgNPh_2$
7	MgH_2 (4.3)	$[i\text{-}Pr(Me)N]_2Mg$ (4.3)	5	Moderately soluble	Crystallized from THF	1.00:0.95	$HMgN\text{-}i\text{-}Pr(Me)$
8	MgH_2 (4.7)	 Mg (4.7)	4	Moderately soluble	Solid crystallized from THF	1.00:0.96	
9	MgH_2 (5.3)	 Mg (5.3)	1	Soluble	Foamy solid	1.00:0.93	
10	MgH_2 (3.8)	$[t\text{-}Bu(Me_3Si)N]_2Mg$	2	Soluble	Foamy solid	1.00:0.94	$HMgN(t\text{-}Bu)SiMe_3$
11	MgD_2 (3.5)	$(n\text{-}Pr_2N)_2Mg$ (3.5)	2	Soluble	Foamy solid	1.00:0.97	$DMgN\text{-}n\text{-}Pr_2$
12	MgD_2 (3.8)	$(i\text{-}Pr_2N)_2Mg$ (3.8)	4	Soluble	Crystalline solid	1.00:0.96	$DMgN\text{-}i\text{-}Pr_2$

was slowly warmed to room temperature with continued stirring and was stirred further at room temperature (for ~10 h) to give a clear solution. The solution was analyzed (Table V) and its infrared spectrum recorded and compared with the spectrum of the (di-*n*-propylamino)magnesium hydride prepared earlier by the redistribution of bis(di-*n*-propylamino)magnesium with MgH_2. Results of similar reactions are given in Table IV.

Preparation of (Diisopropylamino)magnesium Hydride by the Reaction of HMgCl with LiN-*i*-Pr$_2$ in THF. (a) Preparation of HMgCl.[6] To a well-stirred slurry of MgH_2 (4.0 mmol) in THF (20 mL) was added dropwise $MgCl_2$ (4.0 mmol) in THF (30 mL). The reaction mixture was stirred at room temperature for 15 min to give a clear solution. Anal. Calcd for HMgCl: Mg:H:Cl = 1.00:1.00:1.00. Found: 1.00:0.97:1.02.

(b) Reaction of HMgCl with LiN-*i*-Pr$_2$ in THF. A total of 5.0 mmol of HMgCl in THF was allowed to react with LiN-*i*-Pr$_2$ (5.0 mmol) at room temperature. The reaction mixture was stirred for 1 h to give a clear solution. Anal. Calcd for LiCl + HMgN-*i*-Pr$_2$: Li:Mg:H:Cl = 1.00:1.00:1.00:1.00. Found: 1.07:1.00:0.95:1.03. The presence of LiCl was confirmed by the X-ray powder diffraction pattern of the solid obtained when the solvent was removed under vacuum and the presence of HMgN-*i*-Pr$_2$ was shown by comparison of the infrared spectrum of this reaction product with the spectrum of HMgN-*i*-Pr$_2$ prepared by other methods.

Results and Discussion

In our earlier report on the synthesis of (dialkylamino)magnesium hydrides, we showed that these compounds could be prepared by hydrogenation of (dialkylamino)magnesium alkyls (eq 3), $LiAlH_4$ reduction of (dialkylamino)magnesium alkyls (eq 4), and KH reduction of (dialkylamino)magnesium bromide (eq 5). By these methods four compounds, R_2NMgH

$$R_2NMgR' \xrightarrow{H_2} R_2NMgH + R'H\uparrow \qquad (3)$$

$$4R_2NMgR' + LiAlH_4 \rightarrow 4R_2NMgH + LiAlR'_4 \qquad (4)$$

$$R_2NMgBr + KH \rightarrow R_2NMgH + KBr \qquad (5)$$

(where R = Et, *i*-Pr, *n*-Bu, and Ph), were prepared. The difficulty in preparing other (dialkylamino)magnesium alkyls is a result of the instability and resulting disproportionation of these compounds to give bis(dialkylamino)magnesium and dialkylmagnesium compounds (eq 6). Because of this problem

$$2R_2NMgR' \rightarrow (R_2N)_2Mg + R'_2Mg \qquad (6)$$

when some R_2NMgR' compounds were reduced by $LiAlH_4$, a mixture of $(R_2N)_2Mg$ and MgH_2 resulted. Furthermore, this method of reducing R_2NMgR' compounds by $LiAlH_4$ has been found to be limited to the cases where the corresponding products, R_2NMgH, are insoluble in ether, e.g., $(n\text{-}Bu)_2NMgH$ could not be prepared by this method since both the desired product and the by-product ($LiAl\text{-}n\text{-}Bu_4$) are soluble in ether and therefore are difficult to separate. The method involving hydrogenation of R_2NMgR' compounds gave some difficulty in that pure products were not always formed. It was difficult to control hydrogenation such that Mg–N cleavage as well as Mg–C cleavage did not occur. Indeed during the course of hydrogenation of R_2NMgR' compounds, some hydrogenation of the Mg–N bond also occurs leading to products containing H:Mg ratios greater than 1.00.

In order to avoid these complications, we have developed three additional routes for the preparation of (dialkylamino)magnesium hydrides. The first method involves the redistribution of bis(dialkylamino)magnesium compounds with magnesium hydride in THF solvent (eq 7). Bis(dialkylamino)magnesium compounds were prepared in THF by reaction of dialkylamines with dimethylmagnesium in 2:1 molar ratio followed by refluxing the mixture overnight (eq 8). An active form of MgH_2 was prepared by the reaction

$$Mg(NR_2)_2 + MgH_2 \xrightarrow{THF} 2R_2NMgH \qquad (7)$$

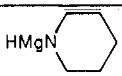
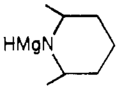
$$2R_2NH + Me_2Mg \rightarrow (R_2N)_2Mg + 2CH_4\uparrow \qquad (8)$$

of diethylmagnesium with $LiAlH_4$ in diethyl ether to form MgH_2, followed by filtration of the insoluble solid and slurrying in THF (eq 9). In this manner, when a THF

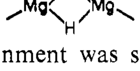
$$Et_2Mg + LiAlH_4 \xrightarrow{Et_2O} MgH_2 + LiAlH_2Et_2 \qquad (9)$$

solution of a bis(dialkylamino)magnesium compound was added dropwise to a well-stirred slurry of MgH_2 in THF, a clear solution resulted. Since MgH_2 is very insoluble in THF, its dissolution in the presence of the bis(dialkylamino)magnesium compound indicates reaction. The elemental analyses of the clear solution in THF indicated that it contained Mg and H in 1:1 ratio (Table I). The infrared spectra of the THF solutions of the (dialkylamino)magnesium hydrides show a medium to strong band in the region 1580–1620 cm^{-1} (Table II). This band has been assigned to Mg–H stretching since it shifted to 1100 cm^{-1} in the deuterio analogues, R_2NMgD. The deuterio compounds, R_2NMgD, were prepared by the reaction of $(R_2N)Mg$ with MgD_2; the MgD_2 was prepared by the reaction of Et_2Mg with $LiAlD_4$ in Et_2O. By comparison of the infrared spectra of R_2NMgH and R_2NMgD it was found that the band at 670 cm^{-1} present in R_2NMgH is shifted to 465 cm^{-1} in the R_2NMgD product indicating that the band at 670 cm^{-1} is due to the Mg–H bending mode. Recently, we

Table II. Infrared Data of (Dialkylamino)magnesium Hydrides

$HMgNEt_2$ (Nujol)	$HMgN$-*n*-Pr_2 (Nujol)	$HMgN$-*n*-Pr_2 (THF)	$DMgN$-*n*-Pr_2 (THF)	$HMgN$-*i*-Pr_2 (Fluorolub)
1560–1620 s, b	1600–1610 m, b	1605 m	1460 m	1610 m
1455 vs	1460 vs	1460 m	1382 m	1460 m
1380 s	1450 vs	1385 m	1365 m	1380 m
1340 sh	1370 vs	1360 m	1150 m, b	1360 m
1168 m	1165 m, b	1156 m, b	1105 s	1275 s, b
1120 m, b	1110 m, b	1030 w	1030 w	1100–1200 s, b
1097 m	1070 m, b	980 m	980 w	1030 m
1035 w, b	1040 m, b	870 w	870 w	965 s, b
990 m	945 m	680 s, b	680 m	900 s, b
865 w	870 wb	575–610 s, b	580–600 m	740 m
720 m	720 m	420 m, b	465 sh, b	650 s, b
580–610 vs, b	610–575 vs, b		420 m, b	580 vs, b
526 vs, b	525 vs, b			500 s
455 sh, b	460 sh, b			430 s
422 b	420 sh, b			385 w
$HMgN$-*i*-Pr_2 (THF)	$DMgN$-*i*-Pr_2 (THF)	$HMgN$-*n*-Bu_2 (THF)	$HMgN$-*sec*-Bu_2 (THF)	$HMgN$-*sec*-Bu_2 (Nujol)
1570–1580 m, b	1478 m	1560–1580 s, b	1570 m, b	1615 m
1478 m	1432 m, b	1435 m, b	1470 sh	1465 vs
1430 m, b	1380 m, b	1375 w	1430 m, b	1455 vs
1380 m, b	1324 w, b	1300 w	1375 s	1445 sh
1320 w, b	1150 m, b	1255 w	1150 m, b	1375 vs
1150 m, b	1100 m	1150 w	975 m, b	1340 sh
980 m	980 m	1130 m	810 sh	1260 w
830 m, b	830 m, b	1105 w	770 m	1150 s
670 s, b	665 m	1075 m	675 s, b	1100–1120 s, b
570 s, b	575 s	1007 m	570 s, b	1030 m
420 m, b	465 s, b	950 w	420 m, b	970 m
	424 m, b	855 w		920 w
		790 m		885 s
		715 m		800 w
		660 s		770 w
		570 s, b		720 s
		410 w, b		610 s
				550–570 vs, b
				500 s, b
				420 sh
$HMgNPh_2$ (Nujol)	$HMgN$(*i*-Pr)Me (Nujol)	 (Nujol)		$HMgN$(*t*-Bu)$SiMe_3$ (Nujol)
1595 sh	1620 sb	1612 m	1605 m	1600 sh
1575 s	1450 vs, b	1465 s	1462 s	1450 vs
1558 sh	1380 vs	1450 vs	1450 vs	1370 vs
1460 vs	1340 sh	1375 vs	1375 vs	1250 vs
1375 s	1200 s	1300 w	1314 m	1190 m
1340 m	1160 s, b	1185 m	1210 w	1032 s
1302 ms	1130 s, b	1145 w	1170 m	1016 sh
1207 m	1035 vs	1005 m	1115 b, m	950 m
1166–1180 m, b	900 s	1045 m	1075 m	865 m
1065 w	795 s	1020 m	1032 m	825 s
1016 m	720 s	890 s	1010 w	770 sh
982 m	580–630 vs, b	852 m	970 sh	746 s
910 sh	520 vs, b	805 m	948 m	720 sh
850 m, b	420 s, b	720 w	872 m	662 w
735 m	385 m	605–580 vs, b	830 b	610 m, b
692 m		470–480 vs, b	790 w	520 m, b
606 m, b		350 m, b	730 sh	
550 m, b			720 m	
500 s			610 sh	
422 m			580 s, b	
370 w			530 s, b	
			500 m, b	

observed the Mg–H stretching mode in HMgX compounds[6] in the region 1250–1300 cm^{-1} and proposed this absorption to be due to



stretching. This assignment was supported by molecular weight data which indicated a dimeric structure. The presence of the Mg–H stretching absorption at a higher position (1580–1630 cm^{-1}) indicates that probably these are terminal Mg–H stretching bands. A Mg–H stretching frequency of 1497 and 1598 cm^{-1} for the $^2\Sigma$ and 2Π states, respectively, has been calculated from the vapor-phase electronic emission spectra of Mg–H.[13] In a similar type of compound of zinc, $HZnN(CH_3)CH_2CH_2N(CH_3)_2$, an infrared band at 1825 cm^{-1} has been reported to be the terminal Zn–H stretching mode.[3]

Molecular weight studies showed that these products, R_2NMgH, are dimeric at infinite dilution; however, the

Table III. X-ray Powder Diffraction Data, *d* Spacings

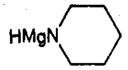
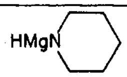
HMgNEt$_2$	HMgN(*i*-Pr)Me	HMgN-*i*-Pr$_2$	HMgN-*sec*-Bu$_2$		HNPh$_2$	
13.8 s 4.52 vw 3.85 vw	9.05 d 7.0 w 5.01 w, d 3.95 vw	9.50 s 5.35 m 3.80 w 3.40 vw	9.51 d, s 3.85 vw	9.25 s 4.6 m 3.62 vw	12.0 s 8.85 w 6.95 w 5.00 m 3.95 s 3.50 w 2.06 w	11.8 m, d 5.25 m 4.00 w

Table IV. Preparation of (Dialkylamino)magnesium Hydrides by the Reaction of R$_2$NH with MgH$_2$

No.	Reactants (mmol)		Reaction time, h	Solubility in THF	Analysis Mg:H	Product
1	MgH$_2$ (4.5)	Et$_2$NH (4.5)	35	Slightly soluble, crystallized from THF	1.00:0.92	HMgNEt$_2$
2	MgH$_2$ (5.3)	*n*-Pr$_2$NH (5.3)	30	Moderately soluble	1.00:0.96	*n*-HMgNPr$_2$
3	MgH$_2$ (5.0)	*i*-Pr$_2$NH (5.0)	25	Moderately soluble	1.00:0.95	*i*-HMgNPr$_2$
4	MgH$_2$ (4.2)	*sec*-Bu$_2$NH (4.2)	24	Soluble, crystallized from THF	1.00:0.95	*sec*-HMgNBu$_2$
5	MgH$_2$ (4.0)	Ph$_2$NH (4.0)	24	Soluble	1.00:0.94	HMgNPh$_2$
6	MgH$_2$ (4.0)	*n*-Bu$_2$NH (4.0)	30	Highly soluble	1.00:0.96	*n*-HMgNBu$_2$

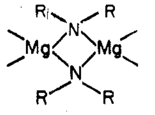
Table V. Molecular Weight Data[a] of (Dialkylamino)magnesium Hydrides

Compd	Concn (molality, *m*) vs molecular association (*i*)					
n-Pr$_2$NMgH	$m = 0.034$	0.071	0.107	0.158	0.192	0.225
	$i = 4.25$	5.48	6.50	7.65	8.34	8.77
i-Pr$_2$NMgH	$m = 0.031$	0.065	0.101	0.133	0.172	0.191
	$i = 2.81$	3.60	4.43	4.55	5.20	5.33
n-Bu$_2$NMgH	$m = 0.035$	0.068	0.105	0.137	0.178	0.223
	$i = 3.86$	5.00	5.82	6.64	7.35	8.03
sec-Bu$_2$NMgH	$m = 0.029$	0.062	0.098	0.134	0.175	0.208
	$i = 3.23$	4.20	5.02	5.51	6.00	6.43
Ph$_2$NMgH	$m = 0.037$	0.073	0.109	0.145	0.185	0.218
	$i = 2.20$	2.30	2.32	2.55	2.80	2.80

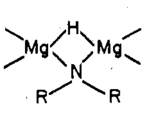
[a] Molecular weight studies were carried out ebullioscopically in refluxing THF at reduced pressure, i.e., 260 mmHg.

molecular association increases with concentration. The compounds with less bulky alkyl groups exhibit more molecular complexity than those compounds with groups having greater steric hindrance. This conclusion is supported by molecular association data which show that the molecular association of the more sterically hindered compounds increases only slowly with an increase in concentration (Table V, Figure 1).

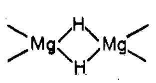
On the basis of infrared spectra and molecular association studies, it is proposed that in these compounds association takes place via both a double-nitrogen bridged species and a mixed nitrogen–hydrogen bridged species. Since the NR$_2$ group is normally a stronger bridging group than hydrogen, it is quite probable that more NR$_2$ groups are involved in bridging than hydrogen. However, it is also possible that more hydrogen atoms are involved in bridging than NR$_2$ groups in those cases where the R groups are sterically bulky groups. In the infrared spectra, the presence of a Mg–H stretching mode suggests that these products contain at least one terminal hydrogen. Although no exact structure can be drawn, it is reasonable to propose that all three possible bonding types (A, B, and C)



A



B



C

exist in solution, but that structure A represents the major species in solution for those compounds where R is not particularly bulky.

An attempt to prepare R$_2$NMgH compounds by the reaction of a dialkylamine with MgH$_2$ in benzene was made earlier[4] but was not successful. During our present investigations we found that R$_2$NMgH compounds could be prepared by the above reaction by replacing the solvent benzene by THF. Our earlier fear[4] that soluble Mg–H compounds might cleave THF was justified in that although R$_2$NMgH compounds do not cleave THF at room temperature over a short period of time (e.g., 1 h), over longer periods of time some THF cleavage is experienced. Thus, when a THF solution of a dialkylamine was added slowly to a well-stirred slurry of MgH$_2$ in THF at low temperature and the temperature allowed to rise to room temperature for 24 h, a clear solution was formed. However, the analysis, of this solution showed that the ratio of hydrogen:magnesium was less than 1 (Table IV) indicating some THF cleavage. This THF cleavage is a result of the long reaction times required for complete reaction. The infrared spectra of these products were found to be similar to the spectra for the products prepared by the redistribution reactions (eq 7).

$$MgH_2 + R_2NH \xrightarrow{THF} R_2NMgH + H_2\uparrow \qquad (10)$$

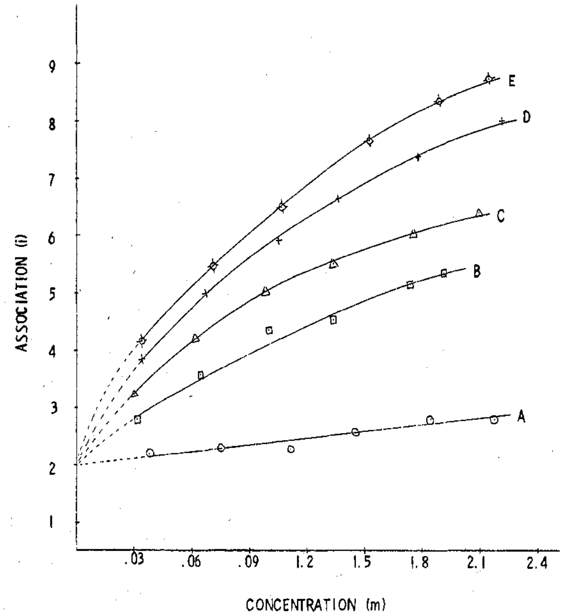


Figure 1. Molecular weight studies of HMgNPh$_2$ (A), HMgN-*i*-Pr$_2$ (B), HMgN-*sec*-Bu$_2$ (C), HMgN-*n*-Bu$_2$ (D), and HMgN-*n*-Pr$_2$ (E) in tetrahydrofuran.

Table VI. NMR Data of (Dialkylamino)magnesium Hydrides in THF (δ, ppm)

HMgN-*n*-Pr$_2$	HMgN-*i*-Pr$_2$	HMgN-*sec*-Bu$_2$	HMgNPH$_2$	HMgN(*t*-Bu)SiMe$_3$	
0.90 (t, Me) 1.44 (q)	0.98 (d, *gem*-Me$_2$)	0.91 (t, 3-Me) 1.01 (d, 2-Me) 1.47 (pentate, methylene)	6.96 (mult, Ph)	1.29 (s, *t*-Bu) 0.06 (s, MeSi)	0.99 (d, 2,6-Me$_2$)

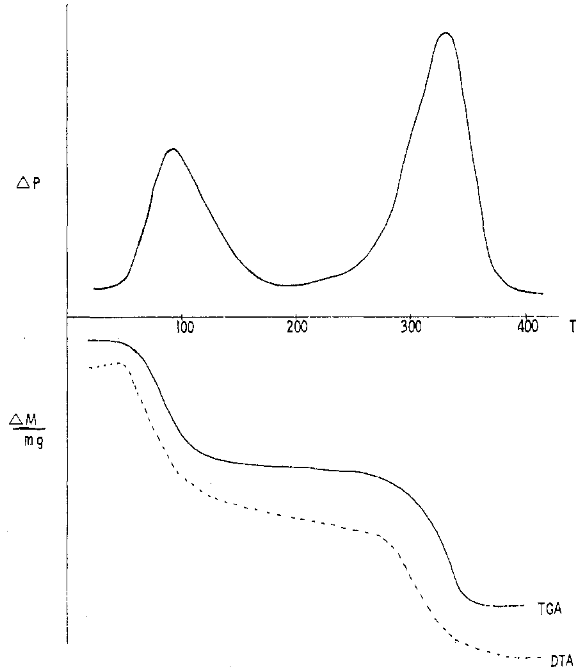


Figure 2. Vacuum DTA–TGA of HMgN-*sec*-Bu$_2$·0.65THF. Heating rate is 4 °C/min.

In preliminary reactions of LiNR$_2$ compounds with HMgCl,[6] it was shown that R$_2$NMgH compounds could be prepared in this manner (eq 11). Although this method does work well and produces pure product, it is not quite as useful as the method based on redistribution of Mg(NR$_2$)$_2$ and MgH$_2$ (eq 7) because of the greater complexity in preparing the starting materials.

$$\mathrm{HMgCl} + \mathrm{LiNR_2} \xrightarrow{\mathrm{THF}} \mathrm{R_2NMgH} + \mathrm{LiCl} \tag{11}$$

The vacuum DTA–TGA of "HMgN-*sec*-Bu$_2$·0.65THF" as a representative compound of this series is shown in Figure 2. The thermogram shows gas evolution at 50–145 (90 °C) and 260–390 (335 °C) with simultaneous weight losses of 24.6 and 27.4%. The data indicate the following pathway (eq 12 and 13) for decomposition. A similar decomposition pathway has been observed in the decomposition of MeMgNR$_2$ compounds.[14] The decomposition mechanism is the subject of considerable effort in our laboratory at the present time.

$$\mathrm{HMgN\text{-}}sec\mathrm{\text{-}Bu_2 \cdot 0.65THF} \xrightarrow{50\text{–}145\ ^\circ\mathrm{C}} \mathrm{HMgN\text{-}}sec\mathrm{\text{-}Bu_2 + THF} \tag{12}$$

$$\mathrm{HMgN\text{-}}sec\mathrm{\text{-}Bu_2} \xrightarrow{260\text{–}390\ ^\circ\mathrm{C}} (\mathrm{MgN\text{-}}sec\mathrm{\text{-}Bu}) + \mathrm{H_2} + \mathrm{C_4H_{10}} \tag{13}$$

In some preliminary experiments involving the reactions of (dialkylamino)magnesium hydrides with cyclic ketones, considerable selectivity has been observed. For example, *n*-Pr$_2$NMgH reduces 2-methylcyclohexanone to give the cis alcohol in 90% yield (the cis alcohol is the least stable alcohol) and it reduces 3,5,5-trimethylcyclohexanone to give the cis alcohol in 98% yield. When the R$_2$NMgH compounds contain more bulky alkyl groups, e.g., *i*-Pr$_2$NMgH and *t*-Bu(Me$_3$Si)NMgH, even more selectivity results. Both *i*-Pr$_2$NMgH and *t*-Bu(Me$_3$Si)NMgH reduce 2-methylcyclohexanone to give the cis alcohol in 98% yield, and they reduce 3,5,5-trimethylcyclohexanone to give the cis alcohol in 99% yield. A detailed study of these compounds with organic substrates is in progress and shall be reported in more detail at a later date.

Acknowledgment. We are indebted to the National Science Foundation (Grant No. MPS 7504127) and the Office of Naval Research (Grant No. N00014-67-A-0419-005AD) for support of this work.

Registry No. (HMgNEt$_2$)$_2$, 66213-34-1; (HMgN-*n*-Pr$_2$)$_2$, 66213-33-0; (HMgN-*i*-Pr$_2$)$_2$, 66213-32-9; (HMgN-*n*-Bu$_2$)$_2$, 66213-49-8; (HMgN-*sec*-Bu$_2$)$_2$, 66213-48-7; (HMgNPh$_2$)$_2$, 66213-47-6; (HMgNMe-*i*-Pr)$_2$, 66213-46-5; (HMgNC$_5$H$_{10}$)$_2$, 66213-45-4; (HMgNC$_5$H$_8$Me$_2$)$_2$, 66213-44-3; (HMgN-*t*-BuSiMe$_3$)$_2$, 66213-43-2; (DMgN-*n*-Pr$_2$)$_2$, 66213-42-1; (DMgN-*i*-Pr$_2$)$_2$, 66213-41-0; MgH$_2$, 7693-27-8; MgD$_2$, 60688-56-4; (Et$_2$N)$_2$Mg, 14167-86-3; (*n*-Pr$_2$N)$_2$Mg, 23293-22-3; (*i*-Pr$_2$N)$_2$Mg, 23293-23-4; (*n*-Bu$_2$N)$_2$Mg, 23293-24-5; (*sec*-Bu$_2$N)$_2$Mg, 65277-27-2; (Ph$_2$N)$_2$Mg, 17711-65-8; (*i*-PrMeN)$_2$Mg, 65277-26-1; (C$_5$H$_{10}$N)$_2$Mg, 16178-51-1; (C$_5$H$_8$Me$_2$N)$_2$Mg, 65277-30-7; (*t*-BuMe$_3$SiN)$_2$Mg, 65277-31-8; *t*-BuMe$_3$SiNH, 5577-67-3.

References and Notes

(1) E. Wiberg and A. May, *Z. Naturforsch., B*, **10**, 234 (1955).
(2) J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 2141 (1960).
(3) N. A. Bell and G. E. Coates, *J. Chem. Soc. A*, 823 (1968).
(4) R. G. Beach and E. C. Ashby, *Inorg. Chem.*, **10**, 906 (1971).
(5) E. C. Ashby and A. B. Goel, *J. Chem. Soc., Chem. Commun.*, 169 (1977).
(6) E. C. Ashby and A. B. Goel, *J. Am. Chem. Soc.*, **99**, 310 (1977).
(7) E. C. Ashby and A. B. Goel, *Inorg. Chem.*, in press.
(8) E. C. Ashby and R. D. Schwartz, *J. Chem. Educ.*, **51**, 65 (1974).
(9) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(10) E. C. Ashby, P. Claudy, J. Bousqet, and J. Etienne, *J. Chem. Educ.*, **52**, 618 (1975).
(11) E. C. Ashby and R. C. Arnott, *J. Organomet. Chem.*, **14**, 1 (1968).
(12) E. C. Ashby and R. G. Beach, *Inorg. Chem.*, **9**, 2300 (1970).
(13) M. A. Khan, *Proc. Phys. Soc., London*, **80**, 523 (1962).
(14) E. C. Ashby, F. Willard, and A. B. Goel, to be submitted for publication.