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THE DIRECT SYNTHESIS OF MAGNESIUM AMIDES AND THE CRYSTAL STRUCTURE OF AN UNUSUAL MAGNESIUM TERT-BUTYLAMIDE

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Summary

The magnesium amides $Mg(NHi\text{-}C_3H_7)_2$; $Mg(N(C_2H_5)_2)_2$ and $Mg(NC_5H_{10})_2$ have been prepared by direct synthesis from magnesium and $i\text{-}C_3H_7NH_2$, $(C_2H_5)_2NH$ or $C_5H_{10}NH$, respectively, at high temperature and under a pressure of hydrogen. When an excess of Mg was used MgH_2 was isolated, suggesting that magnesium hydride is an intermediate in this reaction.

$t\text{-}C_4H_9NH_2$ gave two crystalline products, $NMg_6(NHt\text{-}C_4H_9)_9$ (I) and an insoluble material, probably $(MgNR)_x$. The structure of I was determined by X-ray crystallography.

Introduction

Magnesium amides are known to be formed by reaction of dialkyl magnesium with amine. The complete displacement of the alkyl groups by amino groups is very difficult, and so monosubstituted compounds have usually been isolated. For example, as opposed to the synthesis of many monoamides from secondary amines (reaction 1) [1, 2], the preparation of bis(dimethylamino)magnesium (probably through reaction 2) [1] is the only reported example of isolation of a disubstituted product.

$$MgR_2 + HNR'_2 \rightarrow RMgNR'_2 + RH \qquad (1)$$

$$EtMgNMe_2 \rightarrow \tfrac{1}{2}Mg(NMe_2)_2 + \tfrac{1}{2}MgEt_2 \qquad (2)$$

Our attempts to obtain $Mg(NHi\text{-}C_3H_7)_2$ from diethylmagnesium and iso-propylamine gave products with a N/Mg atomic ratio close to 1.65, with residual metal—carbon bonds [3]; however, $Mg(NHC_6H_5)_2$ was made by reaction of $Mg(C_6H_5)_2$ with aniline [4]. As for other synthetic methods, $Mg(NHC_6H_5)_2$ was prepared by direct reaction of magnesium with aniline at ca. 400°C [5]. Very recently Ashby and Willard [2] reported the preparation of compounds of composition $(MgNR')_x$ by thermal decomposition of $RMgNR'_2$.

TABLE 1

RESULTS OBTAINED FOR THE DIRECT SYNTHESIS OF MAGNESIUM AMIDES FROM MAGNESIUM AND AMINE

Run No.	Reagents		Reaction conditions					Reaction product								
	Magnesium (mmol)	Amine (mmol)	$NaAlH_4$ (mmol)	Solvent (ml)	T(°C)	PH_2 (kg cm^{-2})	Time (h)	Nature[a]	Yield (g)	Chemical composition. Found (calcd.) (%)					IR ν(N—H) (cm^{-1})	RX Powder analysis[b]
										Mg	N	Al	$H_{act.}$ (meq/g)	N/Mg atomic ratio		
1	120	i-$C_3H_7NH_2$ (280)	5	THF (300)	100	180	35	I	16.6	16.9	19.4	0	0	1.99[c]	3220	x
										(17.3)	(19.9)	—	—	(2.00)		
2	150	i-$C_3H_7NH_2$ (350)	7	Toluene (300)	200	210	45	I	20.3	17.6	19.5	0	0	1.92	3220	x
										(17.3)	(19.9)	—	—	(2.00)		
3	190	i-$C_3H_7NH_2$ (170)	9	Toluene (300)	180	200	35	S	9.4	24.8	22.0	1.9	0	1.55	3250	A
								I	3	74.0	6.0	0.9	48	0.13	—	x
4	125	t-$C_4H_9NH_2$ (280)	5	Toluene (300)	200	190	60	C	3.7	18.1	17.3	0	0	1.66	≃3220	x
										(18.0)	(17.3)	—	—	(1.66)[d]		
								R	4	18.3	18.5	2.6	0		≃3220	x
								I	8	18.5	11.0	0	3.3	1.03	—	x
5	130	$(C_2H_5)_2NH$ (300)	6	Toluene (300)	210	200	40	I	6	51.0	11.3	0	—	0.39	—	
								E	2.4	14.0	15.5	—	—	1.92	—	—
										(14.4)	(16.6)			(2.00)[e]		
6	120	$C_5H_{10}NH$ (250)	6	Toluene (300)	180	190	12	S	16	11.5	13.2	—	0	2.03	—	A
										(12.6)	(14.5)			(2.00)[f]		

[a] I = insoluble (or scarcely soluble) material; S = soluble; C = crystals; R = soluble residue to the separation of C; E = product extracted with boiling benzene. [b] x = crystalline; A = amorphous. [c] Calcd. for $Mg(NH i\text{-}C_3H_7)_2$. [d] Calcd. for $NMg_6(NH t\text{-}C_4H_9)_9$. [e] Calcd. for $Mg[N(C_2H_5)_2]_2$. [f] Calcd. for $Mg(NC_5H_{10})_2$.

We describe below the results of attempts to prepare completely substituted magnesium amides by direct synthesis from metal and aliphatic amines.

Results and discussion

Table 1 summarizes the results for the reaction of magnesium with some aliphatic primary and secondary amines. All the reactions were carried out at fairly high temperatures under a pressure of hydrogen. An activator was necessary to promote the reaction; although other activators (e.g. $AlEt_3$, $MgEt_2$) can be used, $NaAlH_4$ was preferred because of its higher activity.

1. *Reaction of magnesium with primary amines*

Isopropylamine reacts with magnesium at high temperature and at ca. 200 kg/cm^2 of hydrogen either in tetrahydrofuran or in toluene to give amides of a composition which depends on the ratio of the reagents. In particular, when isopropylamine was used in stoichiometric amount or in excess for reaction 3, there was a practically quantitative yield (with respect to magnesium) of a product having the expected composition for bis(isopropylamino)magnesium. This crystalline compound is insoluble in the reaction medium and has an IR

$$Mg + 2\ i\text{-}C_3H_7NH_2 \rightarrow Mg(NHi\text{-}C_3H_7)_2 + H_2 \qquad (3)$$

spectrum with ν(N—H) absorption at 3220 cm^{-1}.

With an excess of magnesium, however, a soluble amide was obtained for which chemical analyses indicated an atomic ratio N/Mg close to 1.5 (and the absence of hydride hydrogen). In this case the insoluble residue contained a significant amount of MgH_2, supporting the hypothesis that metal hydride is an intermediate in the synthesis of amides.

The reaction was carried out with other amines in order to obtain a crystalline compound with a similar low N/Mg ratio for a complete molecular characterization. This was achieved with $t\text{-}C_4H_9NH_2$, which reacted with magnesium in toluene to give two crystalline products with different composition, one soluble (N/Mg close to 1.7) and the other insoluble (N/Mg close to 1). When the toluene reaction mixture was concentrated and cooled, crystals separated, which were then subjected to X-ray structural analysis.

This product, to which a formal composition $NMg_6(NHt\text{-}C_4H_9)_9$ (I) can be assigned, has a central nitride nitrogen atom, as would be expected from the reaction of magnesium with ammonia. Reaction 4, with the cleavage of one N—C bond, is the probable pathway for the formation of I under our conditions.

$$4\ Mg(NHt\text{-}C_4H_9)_2 + 2\ Mg + 2\ t\text{-}C_4H_9NH_2 \rightarrow NMg_6(NHt\text{-}C_4H_9)_9 + (CH_3)_3CH + H_2 \qquad (4)$$

Recently thermal cleavage of N—C bonds of magnesium amides from secondary amines to give imides from primary amines was clearly demonstrated by Ashby and Willard (reaction 5) [2], although the reaction proceeds by a different mechanism leading to olefin formation. Although the molecular structure

$$RMgN(CH_2CH_2R')_2 \rightarrow \frac{1}{x}(MgNCH_2CH_2R')_x + CH_2{=}CH\text{—}R' + RH \qquad (5)$$

of the insoluble material with N/Mg ratio close to 1 is unknown, it is likely to be a polymeric imide of magnesium $(MgNR)_x$.

2. *Crystal structure of $NMg_6(NHt\text{-}C_4H_9)_9$*

An irregularly shaped crystal of $NMg_6(NHt\text{-}C_4H_9)_9$ (0.6 × 0.3 × 0.7 mm, approximately), was chosen for crystallographic analysis. From Weissenberg photographs and single crystal diffractometry, the following crystal data were determined: (Cu-$K_{\bar{\alpha}}$, λ = 1.5418 Å) orthorhombic space group *Pbca* (No. 61); *a* 26.603(5), *b* 20.405(3), *c* 19.902(2) Å; $Z = 8$, Dx 0.99 g cm^{-3}.

Diffraction data were collected on a Siemens AED automatic diffractometer, using Ni-filtered Cu-$K_{\bar{\alpha}}$ radiation. A total of 5282 reflections (up to $\theta_{max} = 50°$) were measured, but only 3598 with intensities greater than 2.5-$\sigma(I)$ were used in the solution of the structure and in the subsequent refinement. The structure was solved by direct methods by means of the computer program MULTAN [6] and refined by block-matrix least squares, using anisotropic thermal parameters for magnesium and nitrogen atoms, and isotropic thermal parameters for the carbons. Hydrogen atoms were not refined. The very irregular shape of the crystal prevented the application of an effective correction for absorption (μR — 0.3). The final conventional *R* factor was 0.12.

In the course of the refinement disorder was clearly indicated for the t-C_4H_9 groups, arising from some degree of free rotation around the N—C bonds. Because of the difficulty of assessing the equilibrium positions of these groups, we have used an isotropic thermal factor for the carbon atoms only in the final refinement. This, together with the absorption effect, which, as mentioned, was disregarded, led to a somewhat high value for the final *R* factor. The molecular geometry of the molecule is depicted in Fig. 1. Fractional coordinates are reported in Table 2. Tables with the fractional coordinates of methyl hydrogens and the thermal parameters for all atoms, as well as a list of the structure factors, will be supplied by the authors on request.

The molecular structure $NMg_6(NHt\text{-}C_4H_9)_9$ consists essentially of a nitride atom surrounded by six approximately equidistant magnesium atoms, which are disposed in a nearly perfect trigonal-prismatic geometry. In Fig. 2, the core of the structure and the Mg—N(nitride) bond distances are shown. The regularity of the trigonal prism is shown by both the twist-angle [7] (close to 0°), and the compression ratio [8] (uniformly close to unity).

In addition to the nitride atom, each magnesium atom is tetrahedrically coordinated to three bridging nitrogens, giving rise to nine four-membered (Mg, N(nitride), Mg, N(bridging)) approximately planar rings. Selected mean bond distances are: Mg—N(nitride) 2.148(3) Å (range 2.133—2.174); Mg—N (bridging) 2.093(2) Å (range 2.043—2.125); the latter value is quite similar to the 2.090(4) Å found in $[(THF)Mg(HAlNt\text{-}C_4H_9)_3]$ [9] and to the values of 2.107(3) and 2.102(3) Å observed for $[(CH_3)_2N(CH_2)_2N(CH_3)MgCH_3]_2$ [10]. The intramolecular Mg ... Mg mean distances are 2.82 Å (sides of triangles in the trigonal prism) and 2.80 Å (connectors). The packing shows no critically short intermolecular distances.

3. *Reactions of magnesium with secondary amines*

Bis(dialkylamino)magnesium and bis(cycloalkylamino)magnesium were

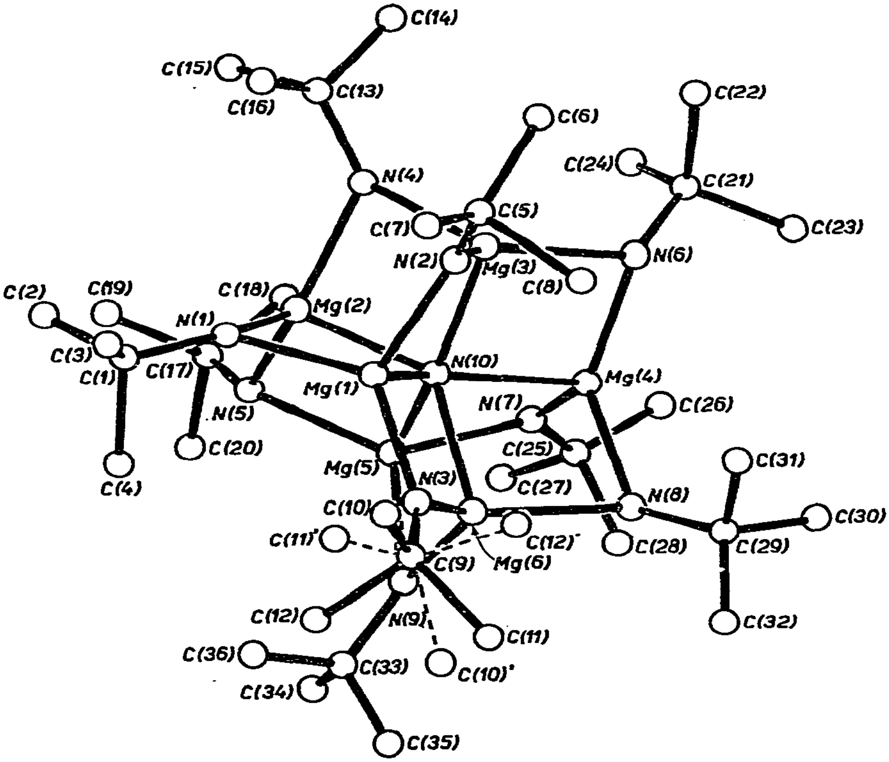
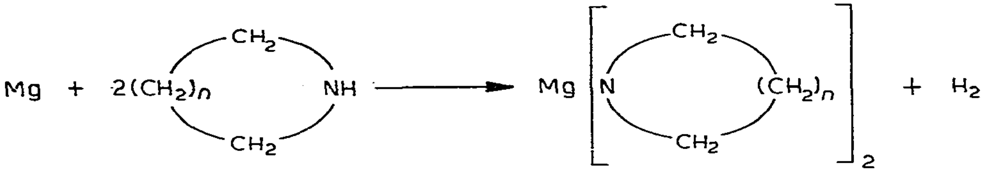


Fig. 1. Perspective view of the $NMg_6(NHt\text{-}C_4H_9)_9$ molecule.

successfully synthesized from diethylamine and piperidine, according to equations 6 and 7.

$$Mg + 2(C_2H_5)_2NH \rightarrow Mg[N(C_2H_5)_2]_2 + H_2 \tag{6}$$



(7)

In the case of diethylamine, the reaction was rather slow. The yield of bis-(diethylamino) magnesium was ca. 11% with respect to amine after 40 h at 210°C and at 200 Kg/cm^2 of H_2. The pure product was separated by extraction with boiling benzene and chemically characterized.

Soluble piperidinomagnesium was obtained in higher yield under less severe conditions. The presence of some hydridic hydrogen in the insoluble residue (also found in the direct synthesis of $Mg[N(C_6H_5)_2]_2$ obtained with a 45% yield after 24 h at 170°C and 190 Kg/cm^2 of H_2) confirms the role of magnesium hydride as intermediate in the direct synthesis of amides.

TABLE 2

FINAL ATOMIC FRACTIONAL COORDINATES ($\times 10^4$) FOR $NMg_6(NHt\text{-}C_4H_9)_9$

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Mg(1)	1871(1)	3854(1)	2344(1)	C(10)′	2183(10)	3838(10)	4581(14)
Mg(2)	1570(1)	4843(1)	1442(1)	C(11)′	2777(11)	3457(14)	3687(14)
Mg(3)	1000(1)	3686(1)	1552(1)	C(12)′	2022(12)	2902(16)	3923(16)
Mg(4)	418(1)	4263(1)	2570(1)	C(13)	1267(4)	4159(5)	13(5)
Mg(5)	998(1)	5419(1)	2459(1)	C(14)	967(8)	3653(11)	—272(11)
Mg(6)	1289(1)	4413(1)	3363(1)	C(15)	1377(7)	4719(9)	—409(9)
N(1)	1269(3)	4399(4)	1638(4)	C(16)	1763(9)	3834(12)	—4(12)
N(2)	1593(4)	3066(4)	1805(5)	C(17)	1253(4)	6366(5)	1210(5)
N(3)	1924(4)	3844(6)	3367(4)	C(18)	760(4)	6171(5)	894(6)
N(4)	1160(3)	4299(4)	730(4)	C(19)	1645(5)	6459(6)	658(6)
N(5)	1408(3)	5837(3)	1673(4)	C(20)	1201(4)	7011(6)	1615(6)
N(6)	275(3)	3502(4)	1887(4)	C(21)	—186(4)	3405(5)	1489(5)
N(7)	216(3)	5243(3)	2396(3)	C(22)	—117(4)	2803(6)	1017(6)
N(8)	542(3)	4127(4)	3595(4)	C(23)	—633(5)	3273(7)	1963(7)
N(9)	1256(4)	5451(4)	3441(5)	C(24)	—275(4)	4010(6)	1073(6)
N(10)	1189(2)	4419(3)	2279(3)	C(25)	—208(4)	5644(5)	2661(5)
C(1)	2774(4)	4657(6)	1641(6)	C(26)	—700(6)	5385(8)	2464(8)
C(2)	2866(5)	5115(7)	1066(7)	C(27)	—144(6)	6357(7)	2486(8)
C(3)	3163(6)	4157(8)	1715(8)	C(28)	—222(7)	5649(9)	3394(9)
C(4)	2779(6)	5108(8)	2295(3)	C(29)	334(5)	3644(6)	4051(6)
C(5)	1694(4)	2389(6)	1741(6)	C(30)	—238(6)	3624(8)	4034(8)
C(6)	1392(5)	2018(7)	1252(7)	C(31)	496(7)	2971(9)	3797(9)
C(7)	2192(7)	2155(9)	1833(10)	C(32)	554(7)	3722(9)	4737(9)
C(8)	1453(8)	2150(10)	2459(11)	C(33)	1489(4)	5940(6)	3839(6)
C(9)	2260(4)	3576(5)	3875(6)	C(34)	1303(6)	6612(8)	3711(8)
C(10)	2598(12)	3058(16)	3703(16)	C(35)	1533(8)	5755(10)	4573(11)
C(11)	2088(15)	3392(19)	4486(20)	C(36)	1981(8)	5963(11)	3606(11)
C(12)	2595(16)	4134(21)	3937(21)				
H(N1)	2291	4089	1245	H(N6)	300	3086	2162
H(N2)	1794	3186	1384	H(N7)	158	5253	1899
H(N3)	2139	4258	3348	H(N8)	403	4535	3787
N(N4)	844	4564	699	H(N9)	906	5469	3675
H(N5)	1725	6004	1890				

Atoms C(10), C(11), C(12), C(10)′, C(11)′, C(12)′ have a site occupation factor of 0.5. Standard deviations in parentheses refer to the last digit.

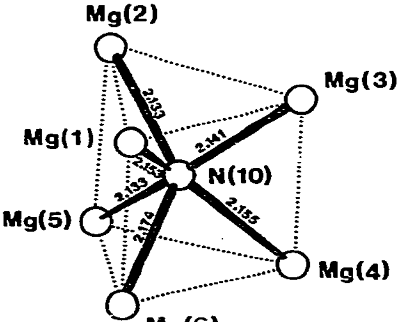


Fig. 2. Coordination geometry around the nitride atom. Average estimated standard deviation = ±0.007 Å.

Experimental

Reagents and solvents

Either pure T7-Walter Marx or MX91-Eckart-Werke powdered magnesium was used indiscrimately after milling for 20 h at room temperature with 2 mole % of $Al(C_2H_5)_3$ in toluene. Before use, $Al(C_2H_5)_3$ was completely removed by filtration. The magnesium was then washed several times with toluene and, eventually, with tetrahydrofuran. $NaAlH_4$ was the Metallgesellschaft pure product. Commercial pure amines and solvents were purified and dried by standard methods. Except for the preparations of amides, which were carried out under a pressure of hydrogen, all operations were carried out under nitrogen.

Chemical and physico-chemical measurements

Chemical analyses were carried out on aqueous solutions prepared by acid decomposition of weighed samples. Al was determined by EDTA-$ZnSO_4$ titration. Mg was titrated directly with EDTA in cooled basic solution; interference from any aluminum present was avoided by complexation with triethanolamine. Hydridic hydrogen was assessed from the amount of hydrogen evolved upon acid hydrolysis. IR spectra were recorded with a Perkin-Elmer 157 spectrometer.

Synthesis of magnesium amides

In addition to the results summarized in Table 1, some typical preparations are described in detail below.

1. Synthesis of magnesium amides from tert-butylamine. A mixture of powdered magnesium (125 mmol), purified as reported above, toluene (300 ml), $NaAlH_4$ (5 mmol) and tert-butylamine (280 mmol) was introduced into a one liter evacuated autoclave equipped with an anchor stirrer. H_2 (135 kg cm^{-2}) was then introduced and the autoclave was heated to 200°C; the pressure rose to ca. 190 kg cm^{-2}. The mixture was stirred under these conditions for 60 h and the autoclave then allowed to cool to room temperature. After removal of hydrogen, the mixture was filtered. After concentration and cooling, crystals (ca. 3.7 g) separated from the solution, and these were dried in vacuo and analyzed (Found: C, 50.8; H, 11.1; Mg, 18.1; N, 17.3; aluminum was absent. $C_{36}H_{90}Mg_6N_{10}$ calcd.: C, 53.4; H, 11.2; Mg, 18.0; N, 17.3%).

The remaining solution was evaporated in vacuo and the residual solid (ca. 4 g) was dried and analyzed (Found Al, 2.5; Mg, 18.3; N, 18.5%).

The insoluble product (ca. 8 g) was dried in vacuo and analyzed (Mg, 18.5; N, 11.0%; H_{act} 3.3 meq/g; aluminum was absent).

2. Synthesis of $(C_5H_{10}N)_2Mg$. A mixture of powdered magnesium (120 mmol), purified as reported above, toluene (300 ml), $NaAlH_4$ (6 mmol) and piperidine (250 mmol) was introduced into a one liter autoclave equipped with an anchor stirrer. H_2 (135 kg cm^{-2}) was then introduced and the autoclave was heated to 180°C; the pressure rose to ca. 190 kg cm^{-2}. The mixture was stirred under these conditions for 12 h and the autoclave then allowed to cool to room temperature. After removal of hydrogen, the mixture was filtered to remove insoluble material and evaporated in vacuo. The residual solid (16 g) was dried in vacuo and analyzed (Found: Mg, 11.5; N, 13.2. $C_{10}H_{20}MgN_2$ calcd.: Mg, 12.6; N, 14.5%).

Acknowledgments

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