

Active Magnesium from Catalytically Prepared Magnesium Hydride or from Magnesium Anthracene and its Uses in the Synthesis¹⁾

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Highly reactive, pyrophoric forms of magnesium with specific surface areas of 20–109 m²/g (Mg*) can be generated by the dehydrogenation of catalytically prepared magnesium hydride (MgH₂) or by decomposition of magnesium anthracene · 3 THF (**4**). The decomposition of **4**, with recovery of anthracene and THF, may be accomplished both thermally and by ultrasound in an organic solvent (toluene, *n*-heptane) or thermally in the solid state in vacuo. Mg* obtained by the latter

method exhibits only weak reflections in the X-ray powder diagram and has, in comparison to other mentioned Mg* species, the highest reactivity toward hydrogen. Diverse Grignard compounds can be prepared under mild conditions (≤25°C) in THF or ether as well as in hydrocarbons by using Mg* from MgH₂ or **4**. The cleavage of THF with formation of 1-oxa-2-magnesiacyclohexane (**2**) is possible by employing Mg* from MgH₂ or **4**.

Activated forms of magnesium have found widespread use in chemical synthesis, particularly for Grignard reactions²⁾, as reducing agents³⁾, for the cleavage of ethers⁴⁾, and in the preparation of magnesium butadiene⁵⁾. With activated magnesium the reactions are usually more efficient, and in some cases new reactions⁶⁾ have been observed. According to Rieke⁷⁾ active forms of magnesium may be prepared by reducing a magnesium halide with an alkali metal, particularly potassium or lithium, in THF or 1,2-dimethoxyethane, if necessary with the addition of naphthalene as an electron-transfer agent^{8,9)}. Vaporization of magnesium leads to a finely divided form¹⁰⁾, which has also been used in various syntheses^{10,11)}.

As has been reported recently¹²⁾, a highly reactive, pyrophoric form of magnesium (Mg*) is obtainable by dehydrogenation of magnesium hydride, which is prepared by catalytic hydrogenation of magnesium using the magnesium anthracene transition-metal halide catalysts¹³⁾ (MgH₂^{*}, Scheme 1)¹⁴⁾. It has also been found that the decomposition of either magnesium anthracene · 3 THF¹⁵⁾ (**4**, Scheme 2) or its homologs, or magnesium butadiene · 2 THF¹⁶⁾ or its homologs results in the generation of Mg*^{14,15a,17)}. In this paper we describe procedures for the generation of Mg* from MgH₂^{*} and **4**¹⁸⁾, the properties of the Mg* species thus prepared, and give examples of their application to the synthesis of Grignard compounds. In addition, the reactivity of Mg* in the cleavage of THF⁶⁾ and toward hydrogen has

been tested. Mg* generated from MgH₂^{*} or **4** has already been used for the dehalogenation of halogenphosphonium halides and dehalogenation/reductive dimerization of halogenazaphosphonium halides²⁰⁾ and tested as a hydrogen- and heat-storage material^{12,21)}. The use of **4** as a stoichiometric source of soluble active magnesium and the application of anthracene as a phase-transfer catalyst for metallic magnesium^{14,17a)} are described in the foregoing paper¹⁾ and reviewed²²⁾ elsewhere.

Generation and Characterization of Mg* from MgH₂^{*} and Magnesium Anthracene · 3 THF (**4**)

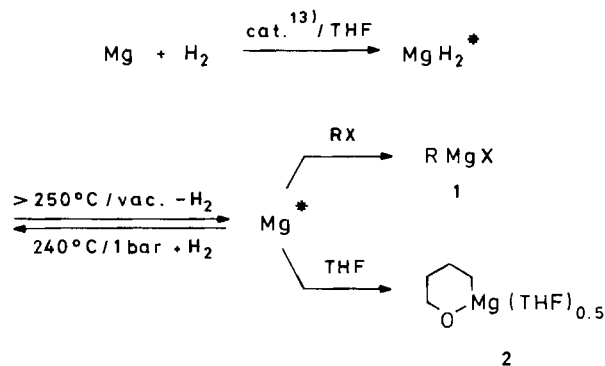
The dehydrogenation of MgH₂^{*} can be performed at temperatures higher than 250°C in vacuo (Scheme 1) or higher than 300°C under normal pressure. The Mg* prepared by dehydrogenation of MgH₂^{*} in vacuo contains small amounts of C, Ti or Cr, MgO (from decomposition of THF), and MgCl₂ and has typically a specific surface area of 20–60 m²/g (Table 2, entries 1–4). For comparison, the Mg species prepared by non-catalytic hydrogenation/dehydrogenation of 270-mesh commercial Mg powder²¹⁾ has a specific surface area of 4.5 m²/g (Table 2, entry 5).

The finding that the reaction of **4** with alkyl halides in solvents like toluene or ether affording Grignard compounds is in fact the result of the reaction of alkyl halides with Mg*, formed from **4** in these solvents¹⁾, has led us to investigate the generation of Mg* by decomposition of **4** in more detail²³⁾. This process may be accomplished in a solvent (procedures a–d) or in the solid form (procedure e).

Heating of **4** in a solvent of low coordinating ability such as toluene or *n*-heptane results in the separation of a volu-

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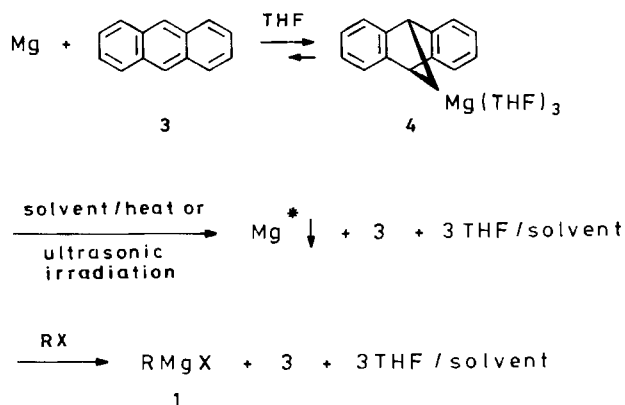
Scheme 1



minous, easily filterable, grey precipitate of Mg^* . Instead of heating, the decomposition of **4** in solution can also be accomplished by ultrasonic irradiation¹⁴. The following procedures a–d have been found suitable for the isolation and/or application of the Mg^* thus generated:

Procedure a: Immediate use of the suspension, i.e. in the presence of anthracene (**3**) and 3 THF, for a chemical, e.g. Grignard reaction (Scheme 2; Tables 4, 5);

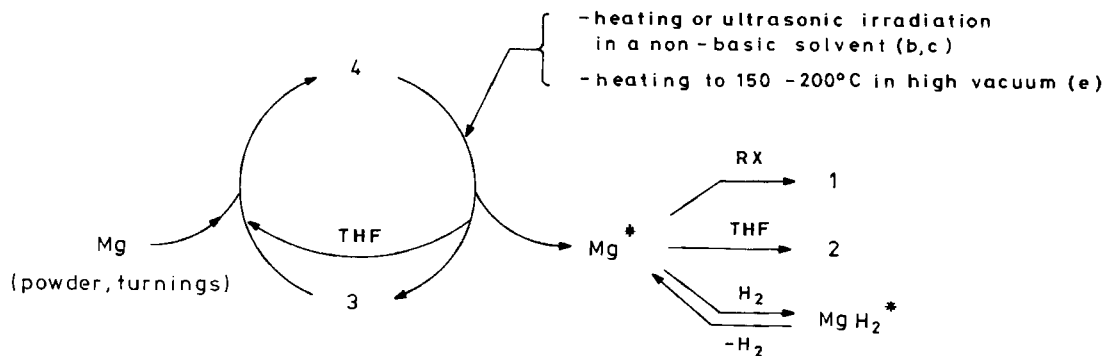
Scheme 2 (Procedure a)



Procedure b: Separation of Mg^* from **3** and THF by filtration (or decantation) and washing; the wet Mg^* is subsequently suspended in either the same or a different solvent (Scheme 3; Tables 6, 7);

Procedure c: After separation from **3** and THF, Mg^* is dried in vacuo and isolated as a grey powder with a specific

Scheme 3 (Procedures b, c, and e)



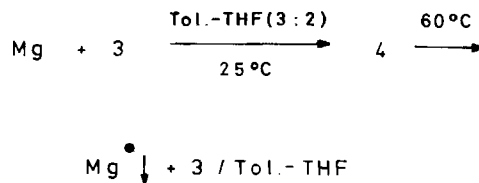
surface area of 13–36 m^2/g , depending on the amount of e.g. toluene used for the decomposition (Scheme 3; Table 2, entries 6–8; Table 8).

According to procedures b and c, **3** and THF contained in the solvent, e.g. toluene, can be separated from the latter by distillation and reused for the preparation of **4**. A batch-wise circular process for the preparation of Mg^* from ordinary Mg powder via **4** can thus be realized (Scheme 3). In a typical experiment concerning the preparation of Mg^* from commercial Mg powder according to procedure c (Scheme 3 and Experimental), 90% of **3** and 70% of THF have been recovered.

Procedure d: The equilibrium between Mg , **3**, THF, and **4** is strongly dependent on both the THF concentration (Table 1)²⁴ and the temperature¹⁵. In a $\approx 3:2$ (vol/vol) toluene/THF mixture at room temperature the formation of **4** is almost quantitative (Table 1), while in the same solvent mixture **4** decomposes at the boiling point.

Due to this fact it is principally possible to prepare Mg^* from Mg powder in a circular process without recurring to the separation of **3** and THF from toluene (Scheme 4). The low rates of formation and decomposition of **4** in such toluene/THF mixtures resulting in Mg^* strongly contaminated with organic decomposition products (Table 2, entry 9) makes, however, this procedure less practicable. Nevertheless, Mg^* generated according to procedure d has proved to be fairly active for the preparation of Grignard compounds (Table 9).

Scheme 4 (Procedure d)



Procedure e: The method which appears to be most suitable for the generation of a highly active Mg^* on a small scale (0.5–1 g) is the heating of the solid **4** to 200°C in high vacuum, whereby THF and **3** sublime and Mg^* remains as a black pyrophoric powder with a specific surface area of 65–109 m^2/g ^{14,17a}) (Scheme 3; Table 2, entries 10, 11; Table 10). It has been observed that Mg^* generated from **4**

Table 1. Dependence of the conversion of anthracene (3) into magnesium anthracene · 3 THF (4) in toluene/THF mixtures on the THF concentration at room temperature^{a)}

THF [vol.-%]	Molar ratio 3:THF	Conversion of 3 into 4 [%]
10	1:3.5	0.2
20	1:7	34.4
30	1:10.5	85.9
40	1:14	97.9
60	1:21	96.0

^{a)} Mg:3 = 3:1; [3]_{initial} = 0.35 mol/l.

which is prepared at 20°C^{15a)} (Table 2, entry 10) in comparison to that generated from 4 which is prepared at 60°C^{15b)} (Table 2, entry 11) has a lower carbon content (4.9 vs. 13.8% C) and weaker reflections in the X-ray powder diagram (below). The lower carbon content of the former Mg* is probably due to the fact that 4 is produced at 20°C in the form of extremely fine crystallites which enable a more complete removal of organic materials during the process of thermal decomposition. The preparation of 4 at 60°C generally leads to the formation of coarser crystals.

The Mg* samples prepared by dehydrogenation of MgH₂ and procedures c, d, and e (Table 2) have also been characterized by X-ray powder diffractometry (Figure 1). The X-ray powder patterns of Mg* samples prepared by dehydrogenation of MgH₂ in vacuo (Ti catalyst, 60°C, Figure 1b; Ti/MgCl₂ catalyst, 60°C; Cr catalyst, 25°C) differ very little from each other and from that of a commercial 270-mesh Mg powder (Figure 1a). A drastic diminution of the reflection peaks, however, is observed with Mg* from 4 prepared at 60°C and decomposed in toluene (procedure c, Figure 1c) and in particular with that decomposed in vacuo (procedure e; Figure 1d). This suggests that the magnesium in these samples is increasingly present in an extremely finely

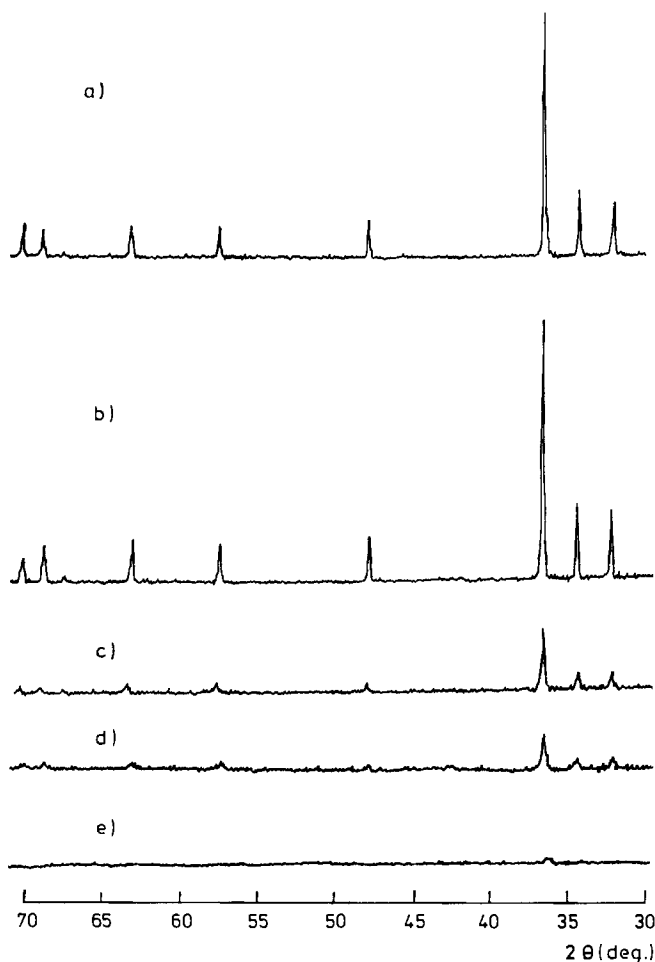


Figure 1. X-ray powder diagrams of various Mg samples (measured in glass capillaries at 0.03°/20 s for 14.8 h): (a) commercial 270-mesh Mg powder, (b) Mg prepared by dehydrogenation of catalytic MgH₂ in vacuo (Ti catalyst, 60°C)^{13a,b)}, (c) Mg* prepared by thermal decomposition of magnesium anthracene (4) in toluene; (d) Mg* prepared by thermal decomposition of 4 in vacuo, using 4 prepared at 60°C; (e) Mg* prepared by thermal decomposition of 4 in vacuo, using 4 prepared at 20°C

Table 2. Data on various active magnesium samples (Mg*) prepared either by dehydrogenation of catalytic (MgH₂) or non-catalytic MgH₂ or by decomposition of magnesium anthracene · 3 THF (4)

Entry	Source of Mg ^{*a)}	Elemental analysis					Spec. surf. Cl area ^{b)} [m ² /g]	X-ray powder pattern	Grignard reaction	Reaction with H ₂ (Fig. 2)
		Mg	C	H	Ti	Cr				
1	MgH ₂ [*] (Ti cat.; 60°C)	96.15	0.0	0.32	0.91	2.11	24.2	Fig. 1b	Table 3	—□—
2	MgH ₂ [*] (TiMgCl ₂ cat.; 60°C)	93.18	0.3	0.52	0.35	4.49	19.7			
3	MgH ₂ [*] (Cr cat.; 60°C)	94.93	1.02	1.01		0.78	2.30			
4	MgH ₂ [*] (Cr cat.; 25°C)	93.18	1.91	1.02		0.66	3.02			
5	MgH ₂ (noncatalytic)						4.5		Table 3	—x—
6	4 (20°C) ^{c)} , procedure c ^{d)}	95.16	3.96	0.80			12.7		Table 8	
7	4 (60°C) ^{e)} , procedure c ^{f)}	91.86	6.16	0.81			23			
8	4 (20°C) ^{c)} , procedure c ^{g)}	95.15	4.00	0.50			35.8	Fig. 1c		—o—
9	4 (20°C) ^{c)} , procedure d	84.14	10.81	1.09			6.7		Table 9	
10	4 (20°C) ^{c)} , procedure e	94.64	4.92	0.35			64.9	Fig. 1e	Table 10	—Δ—
11	4 (60°C) ^{e)} , procedure e	82.66	13.76	3.26			109.3	Fig. 1d		
12	Mg powder (270 mesh)	98.7					0.4 ^{h)}	Fig. 1a		

^{a)} For details of preparation see exp. part. — ^{b)} BET method, N₂. — ^{c)} 4 prepared at 20°C. — ^{d)} 0.7 mol of 4/l toluene. — ^{e)} 4 prepared at 60°C. — ^{f)} 0.29 mol of 4/l toluene. — ^{g)} 0.07 mmol of 4/l toluene. — ^{h)} BET method, krypton.

divided microcrystalline (≤ 50 Å) or amorphous state²⁵). The Mg* generated according to procedure e from **4** which has been prepared at 20 °C (Table 2, entry 10) exhibits only weak reflections in the X-ray powder diagram (Figure 1e). The appearance of only weak reflections persists even after this sample has been subjected to one hydrogenation/dehydrogenation cycle (hydrogenation: 240 °C/1 bar H₂; dehydrogenation: 400 °C, normal pressure; Figure 2).

Synthesis of Grignard Compounds and other Reactions Using Mg* from MgH₂ and **4**

The use of Mg* obtained by dehydrogenation of MgH₂ in vacuo (Table 3) allows the preparation of Grignard compounds in higher yields than the use of ordinary magnesium under mild conditions (e.g. room temperature) and in different solvents, including toluene to which a small amount of THF (Mg*/THF = 1:3; entries 1–3, 8, 10) has been added. The purpose for adding 3 mol of THF/mol Mg* is to allow a comparison with the activity of Mg* prepared in situ from **4** (procedure a, Tables 4, 5). For the preparation of neopentylmagnesium chloride, the entrainment method²⁶ has been used²⁷ since attempts to prepare the reagent by using ordinary magnesium in ether or THF²⁸ have failed²⁷. The application of Mg*, however, allowed neopentylmagnesium chloride to be prepared in ether at room temperature in 86% yield (entry 4). The reaction of Mg* with methallyl chloride in THF (room temperature, 1.5 h) gives methallylmagnesium chloride in 97% yield (entry 5). The same result has also been achieved by using Mg* prepared by subjecting the 270-mesh magnesium powder to a hydrogenation/dehydrogenation cycle (Table 2, entry 5) in the absence of a catalyst (entry 6). For comparison, the reaction of ordinary magnesium with methallyl chloride in ether (10 h, 15 °C) yielded 81% of the Grignard compound and 40% 3-methyl-

3-butenic acid on subsequent reaction with CO₂²⁹), whereas by use of the Rieke magnesium³⁰ (THF, 1 h, 25 °C) 82% of the acid is obtained. Chlorobenzene reacts with Mg* in THF or toluene/THF (60:1 vol/vol) to produce phenylmagnesium chloride in 93 or 94% yield, respectively (entries 7, 8), while application of the Rieke procedure (25 °C, 1.5 h) affords, for the same reaction, 62% benzoic acid after treatment with CO₂³¹). Treatment of 1-chloronaphthalene with Mg* in ether or toluene/THF (60:1 vol/vol) leads to the formation of the Grignard reagent in yields of 94 and 83%, respectively (entries 9, 10), whereas a yield of 76% was achieved²⁶) by means of the entrainment method (ether, at reflux temperature, 12 h).

The utility of Mg* generated according to procedure a (Scheme 2) for the preparation of Grignard compounds is illustrated by the examples listed in Tables 4 and 5. With the exception of propargyl chloride (entry 16), the reaction of all the studied organic halides in toluene (Table 4) with Mg* generated according to procedure a affords high yields of Grignard compounds. Propargyl chloride, however, can be transformed into the Grignard reagent in high yields by reaction with **4** or with ordinary magnesium powder in the presence of **4** in THF¹).

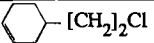
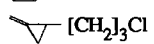
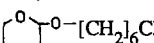
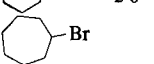
It is known that Grignard compounds may be prepared in hydrocarbon solvents in the presence of THF^{32,33}, Et₂O^{33–35}, NEt₃^{33,36} etc., and as little as one molar equivalent or even less of the Lewis base is needed. Also, in procedure a the presence of THF (Mg*:THF = 1:3) has a positive effect on the yield of Grignard compounds, since when THF is as far as possible removed, as in procedure b, the yields of Grignard compounds become lower (see below). When procedure a is applied the yields of isobutyl-, *sec*-butyl-, *tert*-butyl-, and 1-naphthylmagnesium chlorides (Table 4, entries 2–4, 19) are comparable to or somewhat higher than those when Mg* generated from MgH₂ is used (Table 3, entries 1–3, 10). In comparison to data on the experiment listed in Table 4, entry 2, the yield of the Grignard compound from isobutyl chloride is not significantly changed (89%), when the Mg* suspension is allowed to stand at room temperature for five days, before adding the chloride. With *tert*-butyl chloride the yield of the Grignard compound is 77% when Mg* is generated by ultrasonic irradiation (entry 5) and 81% upon thermal decomposition of **4** (entry 4). (*Z*)- and (*E*)-1-bromopropenes (entries 9, 10) react with Mg* at –30 °C to afford the corresponding Grignard compounds in 79 and 75% yield with 93 and 80% retention of the configuration, respectively, according to the ¹H-NMR spectra of crotonic acids obtained by reaction with CO₂. The standard procedure (THF, 50 °C) yields the Grignard compounds from (*Z*)- and (*E*)-1-bromopropenes with 90 and 80% retention of the configuration, respectively³⁷. Lowering of the reaction temperature and increasing the surface area of magnesium has thus brought no significant improvement to the stereoselectivity of the Grignard reaction. The isomerization during the preparation of Grignard compounds probably takes place via radicals³⁸). While 1-chloro-6-(tetrahydro-2-pyranlyoxy)hexane has been described as exceedingly unreactive toward magnesium in

Table 3. Preparation of Grignard compounds using Mg*^{a)} obtained by dehydrogenation of catalytic (MgH₂) or non-catalytic MgH₂ (r.t. = room temperature)

Entry	RX	Mg*:RX molar ratio	Solvent	React. temp. [°C]	React. time [h]	Yield ^{b)} of RMgX [%]
1	iBuCl	1:1	tol./THF ^{c)}	r.t.	12	83 ^{d)}
2	sBuCl	1:1	tol./THF ^{c)}	r.t.	12	78 ^{d)}
3	tBuCl	1:1	tol./THF ^{c)}	r.t.	12	65 ^{d)}
4	neo-C ₅ H ₁₁ Cl	1:1	ether	20–34	18	86 ^{e)}
5	H ₂ C=C(CH ₃)CH ₂ Cl	1.8:1	THF	24–28	1.5	97 ^{d,e)}
6	H ₂ C=C(CH ₃)CH ₂ Cl	2.2 ^{d)} :1	THF	25–30	2	98 ^{e)}
7	C ₆ H ₅ Cl	1.8:1	THF	21–23	2	93 ^{d,e)}
8	C ₆ H ₅ Cl	1:1	tol./THF ^{c)}	r.t.	24 reflux	2 94 ^{e)}
9	1-chloronaphthalene	2.2:1	ether	r.t.	0.25 reflux	1 94 ^{e)}
10	1-chloronaphthalene	1:1	tol./THF ^{c)}	r.t.	12	83 ^{e)}

^{a)} Except for entry 6, the Mg* from entry 1 of Table 2 was used. —
^{b)} Based on the amount of added RX. — ^{c)} Toluene/THF 60:1 (vol/vol). — ^{d)} According to the MS analysis of the gases evolved upon hydrolysis. — ^{e)} Acidimetric titration of Mg²⁺ upon hydrolysis. —
^{f)} Mg obtained by dehydrogenation of non-catalytic MgH₂ (Table 2, entry 5). — ^{g)} GC analysis of naphthalene produced on protolysis.

Table 4. Use of procedure a for the preparation of Grignard compounds in toluene at room temperature^{a)}; Mg*:RX = 1:1^{a)}

Entry	RX	React. time [h]	Yield of RMgX ^{b)} [%]	Entry	RX	React. time [h]	Yield of RMgX ^{b)} [%]
1	nBuCl	12	87 ^{c)}	11	 [CH ₂] ₂ Cl	2	100 ^{d)}
2	iBuCl	12	85 ^{c)}	12	 [CH ₂] ₃ Cl	3	89 ^{d)}
3	sBuCl	3	81 ^{c)}	13	 [CH ₂] ₆ Cl	12	96 ^{d)}
4	tBuCl	2	81 ^{c)}	14	 Br	96	66 ^{e)}
5 ^{d)}	tBuCl	2	77 ^{c)}	15	Cl[CH ₂] ₄ Cl ^{d)}	12	81 ^{c)}
6	tBuBr	2	72 ^{c)}	16	HC≡CCH ₂ Cl	12	1 ^{e)}
7	neo-C ₅ H ₁₁ Cl	12	78 ^{e)}	17	C ₆ H ₅ Cl	12	78 ^{e)}
8	MeCH=CHBr ^{f)}	48	83 ^{c)}	18	1-chloronaphthalene	2	94 ^{e)}
9 ^{g)}	(Z)-MeCH=CHBr	17	79 ^{h)}	19	p-dichlorobenzene	72	52 ^{k)} 38 ^{l)}
10 ^{g)}	(E)-MeCH=CHBr	12	75 ^{h)}				

^{a)} Unless stated otherwise. — ^{b)} Based on the amount of added RX. — ^{c)} According to the MS analysis of gases evolved on hydrolysis. — ^{d)} Mg* prepared by ultrasonic irradiation of 4 in toluene. — ^{e)} GC analysis of hydrocarbons produced on hydrolysis. — ^{f)} Z/E mixture. — ^{g)} Experiment performed at -30°C. — ^{h)} According to the amount of crotonic acid isolated after carboxylation and hydrolysis. — ⁱ⁾ Acidimetric titration of Mg²⁺ generated by protolysis. — ^{j)} Mg*/RX = 2:1. — ^{k)} Yield of p-ClC₆H₄MgCl on the basis of C₆H₅Cl produced by protolysis. — ^{l)} Yield of p-ClMgC₆H₄MgCl on the basis of C₆H₄ produced by protolysis.

Table 5. Use of procedure a for the preparation of Grignard compounds in *n*-heptane at room temperature: Mg*/RX = 1:1

Entry	RX	React. time [h]	Conversion of RX [%] ^{a)}	Yield of RMgX ^{b)} [%] ^{c)}
1	iBuCl	2	84	83
2	sBuCl	25	89	81
3	tBuCl	19	97	61

^{a)} According to the GC analysis of non-reacted RX. — ^{b)} Determined by MS analysis of gases evolved upon hydrolysis. — ^{c)} Based on the amount of added RX.

Table 6. Use of procedure b for the preparation of Grignard compounds in toluene at room temperature: Mg*/RX = 1:1

Entry	RX	React. time [h]	Conversion of RX [%] ^{a)}	Yield of RMgX ^{b)} [%] ^{c)}
1	iBuCl	12	—	77
2	sBuCl	12	86	56
3	tBuCl	12	—	16

^{a)} According to the GC analysis of unreacted RX. — ^{b)} Determined by MS analysis of gases evolved on hydrolysis. — ^{c)} Based on the amount of added RX.

THF³⁹⁾, the reaction with Mg* according to procedure a in toluene (entry 13) affords the Grignard compound in 96% yield. By reaction with cycloheptyl bromide (entry 14) the Grignard compound is obtained in 66% yield (ref.⁴⁰⁾, ether, at reflux temperature, 20%) and with 1,4-dichlorobutane the yield of the di-Grignard compound is 81% (entry 15)⁴¹⁾.

Isobutyl-, *sec*-butyl-, and *tert*-butylmagnesium chloride are obtained in comparable or somewhat lower yields when,

according to procedure a *n*-heptane is used as the solvent instead of toluene (Table 5).

A comparable yield of isobutyl-, but a substantially lower yield of *sec*-butyl-, and a low yield of *tert*-butylmagnesium

Table 7. Use of procedure b for the preparation of Grignard compounds in *n*-heptane at room temperature: Mg*/RX = 1:1

Entry	RX	React. time [h]	Conversion of RX [%] ^{a)}	Yield of RMgX ^{b)} [%] ^{c)}
1	iBuCl	12	82	83
2	sBuCl	12	62	62
3	tBuCl	12	40	20

^{a)} According to the GC analysis of unreacted RX. — ^{b)} Determined by MS analysis of gases evolved upon hydrolysis. — ^{c)} Based on the amount of added RX.

Table 8. Preparation of Grignard compounds in toluene at room temperature using Mg* obtained according to procedure c; Mg*/RX/THF = 1:1:3

Entry	RX	React. time [h]	Conversion of RX [%] ^{a)}	Yield of RMgX ^{b)} [%] ^{c)}
1	iBuCl	24	78	78 ^{d)}
2	sBuCl	24	—	63 ^{d)}
3	tBuCl	24	100	67 ^{d)}
4	C ₆ H ₅ Cl	96	81	78 ^{d)}
5	1-chloro-naphthalene	96	88	74 ^{d)}

^{a)} According to the GC analysis of unreacted RX. — ^{b)} Based on the amount of added RX. — ^{c)} According to the MS analysis of gases evolved on hydrolysis. — ^{d)} According to the GC analysis of RH produced by protolysis.

chloride are obtained in toluene or *n*-heptane, when procedure b instead of procedure a is applied under comparable conditions (Tables 6, 7). It should be pointed out that, when using this procedure, small amounts of THF will still be present in the solution (Experimental).

Using procedures c or d, we can see that the yields of isobutyl-, *sec*-butyl-, *tert*-butyl-, phenyl- and 1-naphthyl-magnesium chlorides, obtained in toluene in the presence of 3 THF/Mg* (Tables 8, 9), are comparable to those obtained by use of Mg* generated from MgH₂ (Table 3) but lower than those when procedure a (Table 4) is applied.

Table 9. Preparation of Grignard compounds in toluene at room temperature using Mg* obtained according procedure d; Mg*/RX/THF = 1:1:3

Entry	RX	React. time [h]	Conversion of RX [%] ^{a)}	Yield of RMgX ^{b)} [%] ^{c)}
1	<i>i</i> BuCl	12	97	74 ^{c)}
2	<i>s</i> BuCl	12	73	73 ^{c)}
3	<i>t</i> BuCl	12	96	48 ^{c)}
4	PhCl	48	83	76 ^{d)}

^{a)} According to the GC analysis of non-reacted RX. — ^{b)} Based on the amount of added RX. — ^{c)} According to the GC analysis of gases evolved on hydrolysis. — ^{d)} According to the GC analysis of C₆H₆ produced by protolysis.

Isobutyl-, *sec*-butyl-, and *tert*-butyl chloride do not react with ordinary magnesium in hydrocarbons⁴²⁾. The Mg* prepared by procedure e, however, reacts with isobutyl chloride in toluene or *n*-heptane at 70°C to produce isobutylmagnesium chloride (Table 10, entries 1, 2). Treatment of *p*-dichlorobenzene with the same Mg* in the molar ratio of 1:2 in THF affords a mixture of 90% mono- and 10% di-Grignard compound (entry 3). Comparable results have also been obtained by the Rieke procedure, however, only when a molar ratio of *p*-C₆H₄Cl₂/Mg* = 1:4 is used or Mg* is prepared from MgCl₂ and K in the presence of KI³⁰⁾ (Table 10, entries 4, 5).

Table 10. Preparation of Grignard compounds using Mg* obtained according to procedure e

Entry	RX	Mg*/RX		React. temp. [°C]	React. time [h]	Conv. of RX [%] ^{a)}	Yield of RMgX [%] ^{b)}	
		molar ratio	Solvent				1	2
1	<i>i</i> BuCl	1.1:1	toluene	70	2	81	28 ^{c)}	
2	<i>i</i> BuCl	1.0:1	<i>n</i> -heptane	70	2	53	23 ^{c)}	
3	<i>p</i> -dichlorobenzene	2.0:1	THF	25	0.33	100	90 ^{d)}	10 ^{e)}
4 ^{f)}	<i>p</i> -dichlorobenzene	2.0:1	THF	25	0.08	100	86	14
					1	100	86	0
5 ^{f)}	<i>p</i> -dichlorobenzene	4.0:1	THF	25	0.25		90	0
					2		87	13
					2		77	23

^{a)} According to the GC analysis of unreacted RX. — ^{b)} Based on the amount of added RX. — ^{c)} According to the MS analysis of gases evolved on hydrolysis. — ^{d)} Yield of *p*-ClC₆H₄MgCl. — ^{e)} Yield of *p*-ClMgC₆H₄MgCl. — ^{f)} Compiled from ref.³⁰⁾

The cleavage of THF promoted by the Rieke magnesium which results in the formation of **2** has been discovered by Bickelhaupt et al.⁶⁾ and has recently been improved by the application of Ti catalysts⁴⁾. Mg* generated by dehydrogenation of MgH₂ or thermolysis of **4** in vacuo (Schemes 1, 3) slowly reacts with boiling THF to give **2** in 23–25% yield; **2** has been characterized by IR and NMR spectroscopy⁴³⁾ and by its reaction with trimethylsilyl and benzoyl chloride leading to the corresponding trimethylsilyl and benzoyls derivatives, respectively.

As a further measure of the relative reactivity of Mg* samples prepared from MgH₂ or **4**, and in context with the application of active MgH₂/Mg systems as hydrogen- and heat-storage media^{12,21,22)}, the rates and the extent of their uptake of hydrogen at normal pressure/240°C (Figure 2) have been measured^{17a)}. The highest reactivity toward hydrogen among the Mg* samples investigated⁴⁵⁾ (50 and 90% conversion after 1 and 5 h, respectively) is exhibited by the Mg* which shows only weak reflections in the X-ray powder diagram (Table 2, entry 10 and Figure 1e) followed by the Mg* obtained by dehydrogenation of MgH₂^{12,21)} (Table 2, entry 1 and Figure 1b) and magnesium butadiene · 2 THF^{14,17a,19)}.

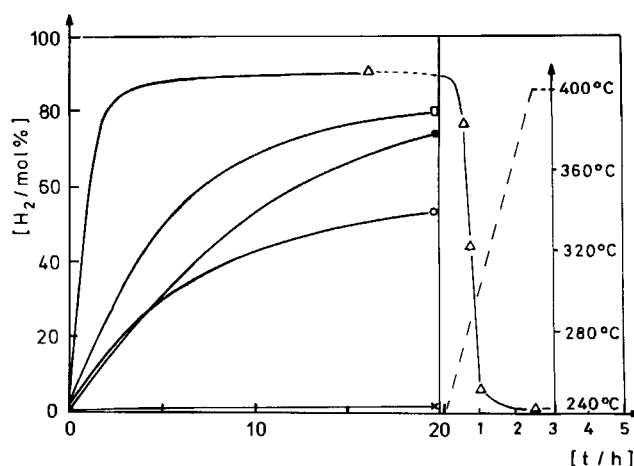


Figure 2. Absorption of hydrogen by various samples of active magnesium (Mg*) at 240°C/1 bar H₂⁴⁴⁾ with time: —△—, Mg* prepared by thermal decomposition of magnesium anthracene (**4**) in vacuo, using **4** prepared at 20°C; —□—, Mg* prepared by dehydrogenation of catalytic MgH₂ in vacuo (Ti catalyst, 60°C)^{13a,c)}; —●—, Mg* prepared by thermal decomposition of magnesium butadiene in toluene¹⁹⁾; —○—, Mg* prepared by thermal decomposition of **4** in toluene; —×—, Mg* prepared by dehydrogenation of non-catalytic MgH₂ in vacuo

The results presented in this paper suggest that magnesium species (Mg*) accessible by dehydrogenation of catalytically prepared magnesium hydride¹³⁾ (MgH₂) or decomposition of magnesium anthracene · 3 THF¹⁵⁾ (**4**) are highly reactive and therefore suitable for synthetic applications such as the preparation of Grignard reagents, dehalogenations, and reductive dimerizations²⁰⁾ etc.¹⁴⁾ In this respect they are comparable to the Rieke^{2,7–9)} or vaporized^{10,11)} magnesium. The Mg* species described in this paper differ, however, from those prepared according to known^{7–11)} methods in so far as they can be prepared free of solvents

and alkali metal, or alkali metal halides. The highest reactivity among the Mg^* species investigated in this article seems to be associated with the solid isolated according to procedure e, while procedure a appears to be most effective for the application of Mg^* in organic solvents.

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Experimental

1H NMR: Bruker WH-400. — ^{13}C NMR: 75.4 MHz, Bruker WM-300. — IR: Nicolet 7000. — MS: CEC-103 mass spectrometer. — GC/MS: F-22 Perkin Elmer gas chromatograph, combined with a CH-7-A mass spectrometer. Conditions for the GC analysis: 25 m OV 1 column, temperature 100–280 °C (8 °C/min), H_2 carrier gas, FID. — X-ray powder spectra: STAD/2/L powder diffractometer (STOE), graphite monochromator (Cu- $K_{\alpha 1}$ line). — The specific surface areas were measured by the BET method with nitrogen (Accusorb 2100 E, Micromeritics). — Elemental analyses: Dornis & Kolbe, Mülheim-Ruhr.

All reactions and operations were carried out under argon in air- and water-free solvents. THF was heated at reflux over $MgEt_2$ and distilled. Toluene was dried over $NaAlEt_4$. If not stated otherwise, Mg powder 270-mesh, PK-31, from the Eckart-Werke was used. Anthracene (Rütgerswerke AG, 99%) was employed without further purification. Organic halides were dried over P_2O_5 , distilled, and stored over molecular sieves (4 Å) under argon.

Mg^* from MgH_2 : The 3-l stainless-steel container (Figure 3) was charged with 432.0 g of MgH_2 prepared by catalytic hydrogenation of magnesium powder ($TiCl_4/Mg$ anthracene catalyst, 50–65 °C/5 bar) in place of the $CrCl_3/Mg$ anthracene catalyst^{13a,13c}; Table 2, entry 1). The container was inserted into an electrically heated oven and connected to a series of three traps, an oil vacuum pump, and a gas flowmeter (Figure 4). The first trap was kept at room temperature, and the second and third traps were cooled with dry ice/acetone. The hydrogen evolution was registered by the gas flowmeter and the temperature of the oven recorded on a two-channel plotter (Figure 5). The hydride was heated in vacuo at about 1 °C/min from room temperature to 370 °C, and this temperature was maintained until no further H_2 evolution was noted (Figure 5, —). The dehydrogenation started at about 250 °C (oven temperature); the maximum dehydrogenation rate was approximately 2 l H_2 /min (Figure 5, - - -). Organic materials which sublimed into the H_2 stream were collected in three traps (the first trap also collected MgH_2 removed from the container in the H_2 stream). The process of programmed heating/dehydrogenation was completed within ≈ 12 h with the evolution of 393.8 l of H_2 (20 °C, 1 bar) (Figure 5), corresponding to 33.08 g of H_2 (7.66 wt-% of the starting material). The container was allowed to cool to room temperature and the fine grey pyrophoric (*caution!*) Mg^* powder (384.6 g) transferred to the steel container shown in Figure 6 and stored under argon. The dehydrogenations of MgH_2 prepared by using the $TiCl_4/MgCl_2/Mg$ -anthracene catalyst at 60 °C^{13d,13e} or the $CrCl_3/Mg$ -anthracene catalyst^{13a,13c} at 25 °C (Table 2, entries 2–4) were carried out analogously. The data concerning Mg^* species obtained by dehydrogenation of MgH_2 are presented in Table 2.

Non-catalytic Hydrogenation of Mg Powder and Dehydrogenation of the Resulting MgH_2 ^{2b}: 39.99 g (1.65 mol) of Mg powder was placed into a steel autoclave fitted with a glass vessel. The autoclave was evacuated twice (0.1 mbar) at room temperature and pressur-

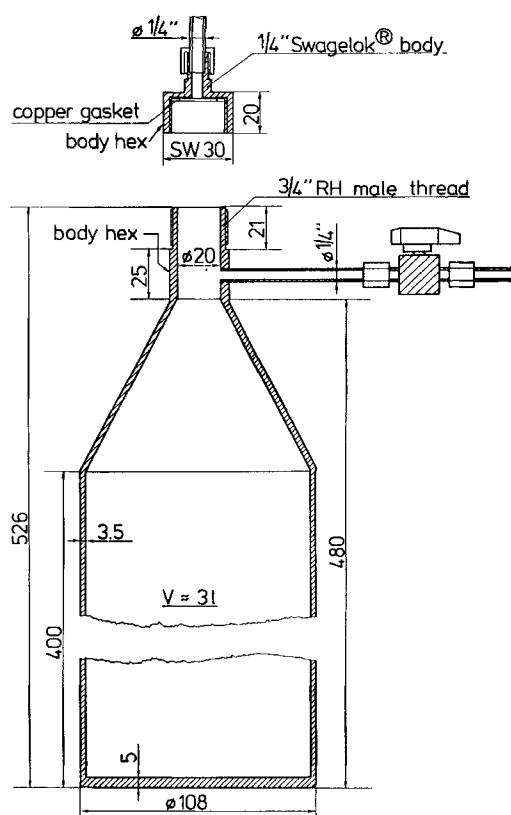


Figure 3. Stainless steel container used for dehydrogenation of MgH_2 powder in vacuo to produce active magnesium

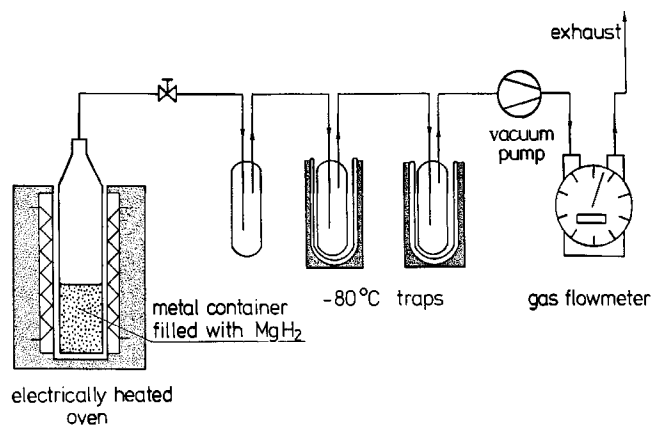


Figure 4. Experimental setup for dehydrogenation of MgH_2 powder in vacuo

ized with 3 bar H_2 . The H_2 pressure was increased to 5 bar, and the autoclave heated to 345 °C (oven temperature), and at that temperature the H_2 pressure was then increased to 15 bar and maintained constant until completion of hydrogenation (≈ 24 h), resulting in an uptake of 7.47 wt-% of H_2 (with respect to MgH_2). The MgH_2 was dehydrogenated to an activated form of magnesium (Table 2, entry 5) at 383 °C (oven temperature) under normal pressure with the evolution of 7.49 wt-% of H_2 (with respect to MgH_2) in the course of 1.5 h.

Procedures a and b for the generation of Mg^* are described below in context with their use in the preparation of Grignard compounds.

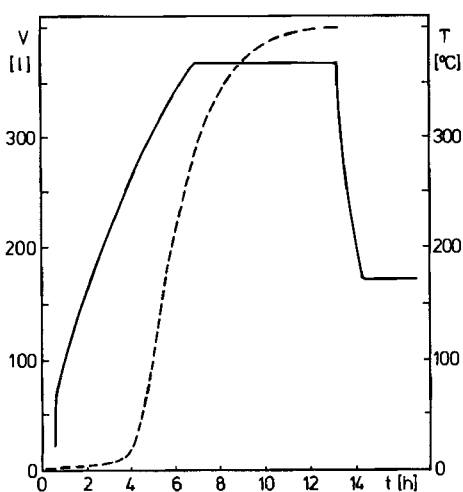


Figure 5. Hydrogen evolution (---) during dehydrogenation of catalytic MgH_2 in vacuo as a function of (oven) temperature (—) and time

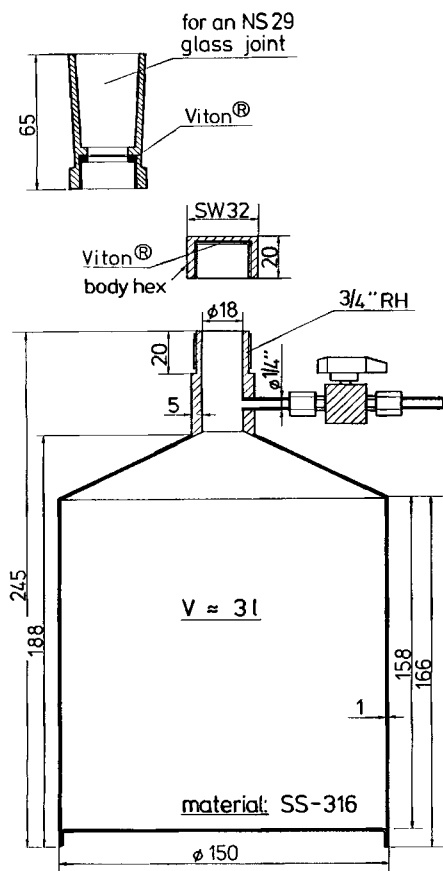


Figure 6. Steel container used for the storage and transportation of air-sensitive powders or liquids, for instance MgH_2 or active magnesium; upper part of Figure 6: piece for connecting the 3/4" male-threaded steel container to an NS 29 glass joint for handling MgH_2 or active magnesium under inert gas (argon)

Procedure c; 0.7 mol of 4/l Toluene: 223.0 g (0.53 mol) of **4**, prepared at 20°C as previously described^{15a}, was suspended in 750 ml of toluene and the suspension stirred and heated to 100°C until **4** was completely decomposed (≈ 1 h). The hot suspension was filtered, washed with hot (90–100°C) toluene (3 \times 0.6 l) and dried

at 70°C in high vacuo. Yield of Mg^* : 12.41 g (96%; Table 2, entry 6, and Table 8).

Procedure c; 0.29 mol of 4/l Toluene: A 10-l three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer was charged with 7.5 l of toluene. The toluene was heated to 60°C by means of an oil bath and with constant stirring at that temperature. 898.4 g (2.16 mol) of **4**, prepared according to ref.^{15b}, was given in portions into the flask. After further heating and stirring, the color of the suspension turned yellow at about 100°C and grey at about 105°C. When the stirring was stopped, Mg^* settled on the bottom of the flask as a voluminous, fluffy grey precipitate. The decomposition of **4** took 75 min from the time **4** was added. 5 l of the hot, clear supernatant solution was siphoned off and the rest of the suspension filtered at 80°C through a metallic pressure filter (diameter 30 cm; filter cloth: polypropylene cloth, 530 g/m², Verseidag Co.), applying an argon overpressure of 0.4 bar. The filtration was completed within 5 min. The Mg^* on the filter was washed three times with 1.2 l of hot (70°C) toluene and dried in vacuo (0.2 mbar). Yield: 56.16 g (97%) of Mg^* (Table 2, entry 7) as a grey powder. The filtrate (8.5 l) was fractionally distilled on a 1.5-m column filled with glass rings (diameter 6 mm) to separate THF from toluene and **3**. The first fraction (60–80°C, 309.9 g) contained 85.4% THF and 14.6% toluene and the second (80–110°C, 284.4 g) 16.7% THF and 83.3% toluene (GC analysis). The toluene was separated from **3** by distillation in vacuo (45–55°C/100–130 mbar) and subsequent drying of **3** in vacuo (0.2 mbar/room temp.) resulting in 7.7 l of toluene of 99.4% purity (rest THF) and 348.1 g of **3** (90% recovery). The toluene used as a washing liquid (3.8 l) contained 0.8% THF and 0.7% **3** (23 g). Taking into account the amount of THF contained in the first and second fraction (321.7 g), 70% of the THF was recovered (rest of THF being found in the recovered 7.7 l toluene (≈ 40 g), and the toluene used as a washing liquid (≈ 26 g).

Procedure c; 0.06 mol of 4/l Toluene: 12.88 g (30.7 mmol) of **4**, prepared at 20°C as described previously^{15a}, was suspended in 500 ml of toluene. The suspension was stirred and heated from room temp. to 70°C within 20 min. At room temp. the suspension became green, at 40°C it turned greyish-green, and at 60°C the precipitate turned grey, and the solution became colorless. The hot suspension was filtered, and Mg^* washed with toluene (2 \times 10 ml) and pentane (2 \times 10 ml) and dried in high vacuo. Yield: 0.79 g. The data on the Mg^* thus obtained are presented in Table 2, entry 8.

Formation of 4 in Toluene/THF Mixtures at Room Temperature (Table 1): In each case 15.60 g (87.5 mmol) of **3**, 6.38 g (263 mmol) of Mg powder (50 mesh), and 0.1 ml of EtBr were stirred in 250 ml of the particular toluene/THF mixture at room temp. for 5 d. Thereafter, 1.0 ml of each suspension was decomposed by adding 5 ml of toluene/ CH_3OH (25:1 vol/vol) and the conversion of **3** into **4** calculated from the gas-chromatographically determined 9,10-dihydroanthracene/**3** ratio¹⁵. The results are listed in Table 1.

Procedure d. Formation of 4 in Toluene/THF 3:2 (vol/vol) at Room Temperature: 200 g (1.12 mol) of **3**, 24.30 g (1.0 mol) of Mg powder in a mixture of 0.6 l of toluene and 0.4 l of THF, after the addition of ≈ 0.5 g **4**, were magnetically stirred (800–1000 r.p.m.) at room temp. for 7 d. Decomposition of **4** and isolation of Mg^* : The suspension of **4** in the stirred toluene/THF mixture was heated to 90°C until the orange color of **4** had disappeared (≈ 2 h), the hot grey suspension was filtered (D3 frit) and the filter cake (Mg^*) washed with 3 l of hot toluene. After drying for 20 h in high vacuo at 90°C, 22.13 g of Mg^* was obtained as a grey powder. The data concerning this Mg^* are given in Table 2, entry 9.

Procedure e; Mg from 4 Prepared at 20°C:* In a typical experiment 13.37 g of **4**, prepared at 20°C as previously described^{15a)}, was placed into a 250-ml two-necked flask connected to a high vacuum line by a glass elbow fitted with a glass frit (to prevent suction of Mg* dust from the flask). Under high vacuum the flask was first heated (oil bath) at 80°C for 4 h, in the course of which mainly THF was eliminated and condensed in a receiver cooled with liquid nitrogen. Then the temperature was increased to 200°C for 5 h, in the course of which the sublimation of **3** occurred. After the thermal decomposition was complete, 83% of THF was found in the receiver which was cooled with liquid nitrogen, and 82% of **3** was recovered as sublimate (GC analysis). The residue (760 mg) was Mg* as a fine and highly reactive pyrophoric black powder. The elemental composition and other data concerning this Mg* are given in Table 2, entry 10. The experiments involving the generation of Mg* by thermal decomposition of **4** were performed several times and are well reproducible. In most of the experiments, in between heating at 80 and 200°C, the sample was also heated at 150°C for 2–4 h. The carbon content of the resulting Mg* samples varied between 5 and 7% and the specific surface area between 60 and 75 m²/g.

Procedure e; Mg from 4 Prepared at 60°C:* The experiment was performed with 11.30 g of **4**, prepared at 60°C^{15b)} in an analogous way as the one described above. The flask was heated at 80°C for 3 h, at 150°C for 4.5 h, and at 200°C for 7 h in order to produce 596 mg of Mg* (Table 2, entry 11).

Preparation of Grignard Compounds Using Mg Obtained by Dehydrogenation of Catalytic (MgH₂) or Non-catalytic MgH₂ (Table 3):* With the exception of entry 6 (Mg from non-catalytic MgH₂) in the experiments of Table 3, Mg* from entry 1 of Table 2 was used.

Table 3, Entries 1–3, 8, 10: A solution of an equimolar amount of the respective organic halide in 30 ml of toluene was added dropwise with stirring at room temp. for 0.5 h to a suspension of 0.30 g (11.9 mmol) of Mg* in a mixture consisting of 150 ml of toluene and 3 ml of THF (3 THF/Mg*). The mixture was stirred for the time and at the temp. given in Table 3. The yield of the respective Grignard compound was determined by removing the solvent in vacuo, hydrolysis of the residue, and determination of the gases evolved in the MS analysis and of naphthalene formed in the GC analysis.

Table 3, Entry 4: To a suspension of 7.60 g (0.30 mol) of Mg* in 150 ml of ether was added dropwise and with vigorous stirring for 2.5 h a solution of 29.82 g of (0.28 mol) neopentyl chloride in 50 ml of ether, causing the ether to reflux. The mixture was stirred for ca. 12 h and then filtered to remove the unreacted Mg*. According to the acidimetric titration of an aliquot of the solution after hydrolysis the yield of neopentylmagnesium chloride was 86%.

Table 3, Entry 5: To a suspension of 0.56 g (22.1 mmol) of Mg* in 50 ml of THF was added dropwise, by means of a syringe and with stirring for 20 min, 1.22 ml (1.13 g; 12.5 mmol) of methallyl chloride (purity 96.9%, 0.04% H₂O, according to GC analysis). During the addition of the methallyl chloride the temperature of the reaction mixture was maintained between 24 and 28°C. The suspension was stirred for an additional 1.5 h and filtered. According to the acidimetric titration of magnesium and the amount of isobutene evolved (MS analysis) upon hydrolysis of the residue obtained by evaporation of an aliquot of the solution in vacuo, the yield of methallylmagnesium chloride was 97%.

Table 3, Entry 6: To a suspension of 0.58 g (23.9 mmol) of Mg prepared by non-catalytic hydrogenation/dehydrogenation of Mg powder (Table 2, entry 5; p. 1523) in 50 ml of THF was added an iodine crystal and, thereafter, dropwise and with stirring for 30 min

a solution of 1.05 ml (10.6 mmol) of methallyl chloride in 10 ml of THF. During the addition of the methallyl chloride the temperature of the reaction mixture was maintained between 21 and 30°C. The suspension was stirred at room temp. for an additional 2 h and filtered. According to the acidimetric titration of an aliquot of the solution after hydrolysis, the yield of methallylmagnesium chloride was found to be 98%. For comparison, an experiment analogous to that described above, and performed by use of the 270-mesh Mg powder (Table 2, entry 12), gave methallylmagnesium chloride in only 46% yield.

Table 3, Entry 7: 1.27 ml (1.40 g, 12.4 mmol) of chlorobenzene (water content 0.02%, determined by GC analysis) was added to a stirred suspension of 0.57 g (22.5 mmol) of Mg* in 50 ml of THF by means of a syringe for 30 min. During the addition the temp. of the reaction mixture was kept between 21 and 23°C. After stirring at room temp. for an additional 2 h the suspension was filtered. On the basis of the acidimetric titration of magnesium and the amount of benzene formed upon protolysis of an aliquot of the solution (GC analysis, *n*-C₈H₁₈ as internal standard) the yield of phenylmagnesium chloride was 93%. In addition, 0.2 mmol (1.4%) of unreacted chlorobenzene was detected in the solution by GC analysis.

Table 3, Entry 9: To a suspension of 2.90 g (11.5 mmol) of Mg* in 50 ml of ether was added, by means of a syringe, in 3–4-ml portions with constant stirring for 45 min a solution of 6.80 ml (8.13 g, 50 mmol) of 1-chloronaphthalene (99.7% pure and water-free, according to GC analysis) in 50 ml of ether. During the addition of 1-chloronaphthalene the temp. of the reaction mixture was maintained between 22 and 27°C and a white voluminous solid precipitated from the solution. After stirring at room temp. for 15 min, 50 ml of ether was added and the mixture heated under reflux for 1 h. 10.0 ml of the suspension (total amount 157 ml) was filtered and the excess of Mg* washed with ether and THF. According to the amount of naphthalene formed upon protolysis of the filtrate (GC analysis, *n*-C₁₆H₃₉ as internal standard), the yield of 1-naphthylmagnesium chloride was 94%. Unreacted 1-chloronaphthalene was not detectable in the solution.

*Preparation of Grignard Compounds in Toluene (Table 4) or *n*-Heptane (Table 5) Using Procedure a:* With the exception of entry 5, Table 4, Mg* was generated by heating a stirred suspension of 4–6 g (10–15 mmol) of **4** in 150 ml of toluene or *n*-heptane to 90°C until the decomposition of **4** was complete (toluene ≈ 20 min, *n*-heptane ≈ 1.5 h). In experiment 5 of Table 4 the decomposition of 4.80 g (11.5 mmol) of **4** in 150 ml of toluene was performed by ultrasonic irradiation of the suspension in a water bath for 50 min. To the Mg* suspension was added dropwise with stirring at room temp. for 0.5 h (exception: experiments of the entries 9 and 10, Table 4) a solution of an equimolar amount of the respective organic halide in 30 ml of toluene or *n*-heptane. The mixture was stirred at room temperature for various times given in Tables 4 and 5. The yields of the Grignard compounds and the methods used for their determination are listed in Tables 4 and 5.

In the experiments 9 and 10 of Table 4, (*Z*)- and (*E*)-1-bromo-1-propenes (99.7 and 98.5% purity, respectively, GC analysis) in toluene were added to the Mg* suspension at –30°C, and this temp. was maintained over a period of 17 and 12 h reaction time, respectively. The flasks were then evacuated, and CO₂ (1 bar) was introduced at –30°C with stirring into the flasks from a gas buret until the CO₂ absorption was completed (25–30 min). The solvent was then removed in vacuo, the residue hydrolyzed by the addition of H₂O and 10 ml of 0.1 N HCl, the aqueous layer extracted several times with ether, the combined ether extracts were dried with CaCl₂,

and the ether was removed in vacuo. The yields of the Grignard compounds in Table 4 are given on the basis of the amounts of the stereoisomeric mixtures of (*Z*)- and (*E*)-crotonic acids thus obtained. The ratios of the stereoisomers of the acids were determined from the ratio of the intensities of the signals of their methyl protons in the $^1\text{H-NMR}$ spectrum (CDCl_3 , 200 MHz).

Preparation of Grignard Compounds in Toluene (Table 6) or *n*-Heptane (Table 7) Using Procedure b: The generation of Mg^* by heating 10–15 mol of **4** in 150 ml of toluene or *n*-heptane was performed in the same way as described for procedure a. The precipitated Mg^* was allowed to settle down, and as much as possible of the clear supernatant solution was carefully removed by means of a siphon. 50 ml of fresh toluene (*n*-heptane) was added to the precipitate, the suspension stirred for 5 min, and the solution again siphoned off. This operation was repeated once. The Mg^* was then suspended in 100 ml of fresh toluene (*n*-heptane), and a solution of an equimolar amount of the respective organic halide in 30 ml of toluene (*n*-heptane) was added dropwise to the stirred suspension at room temp. for 0.5 h. The mixture was stirred at room temp. for an additional 12 h. The volatiles were distilled off in vacuo (0.2 mbar), the residue was hydrolyzed by the addition of water and the gases (3–12% THF, 5–60% H_2 , rest *n*- or *i*- C_4H_{10}) analyzed by mass spectrometry. The distillate was analyzed for unreacted RX by GC analysis.

Preparation of Grignard Compounds in Toluene (+3 THF/ Mg^*) Using Mg^* Obtained by Procedures c (Table 8) or d (Table 9): 10–15 mmol of Mg^* obtained by procedure c (Table 2, entry 6) or d (Table 2, entry 9) was suspended in 50 ml toluene and 3 THF/ Mg^* (2.5–3.5 ml THF) added. To the suspension was then added dropwise with stirring at room temp. for 0.5 h a solution of an equimolar amount of the respective organic halide in 20 ml of toluene. The mixtures were stirred at room temperature for times given in the Tables 8 and 9. The volatiles were removed in vacuo, the residue was hydrolyzed by the addition of water, and the gases evolved were analyzed by mass spectrometry. In the case of phenyl- and 1-naphthylmagnesium chloride the yields of the Grignard compounds were determined by GC analysis of the benzene and naphthalene formed on hydrolysis. The distillate was analyzed for unreacted RX by GC analysis.

Preparation of Grignard Compounds Using Mg^* Obtained by Procedure e (Table 10)

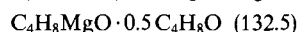
Entry 1: A solution of 2.30 g (24.7 mmol) of *i*- $\text{C}_4\text{H}_9\text{Cl}$ in 30 ml of toluene was added dropwise to a stirred suspension of 0.68 g of Mg^* (Table 2, entry 10; 26.5 mmol) in 70 ml of toluene at room temp. for 20 min. After the addition was complete, the mixture was heated to 70°C and stirred for 2 h. The suspension was filtered, and the filter cake washed with pentane and dried in vacuo (0.2 mbar) to yield 1.69 g of a solid having the composition C 32.2, H 5.4, Mg 26.4, Cl 35.9% (Mg/Cl = 1:1). Protolysis of 388.3 mg of this solid with 2-ethyl-1-hexanol followed by 5 N H_2SO_4 produced 57.0 ml of gas (20°C, normal pressure). The composition of the gas (MS analysis) was: *i*- C_4H_{10} 69.6, H_2 30.4%. On the basis of the *i*- C_4H_{10} content a 34.3% yield of isobutylmagnesium chloride with respect to the converted *i*- $\text{C}_4\text{H}_9\text{Cl}$ (below) was calculated. GC-MS coupling analysis of the toluene filtrate gave the following results: 0.44 g (4.8 mmol) of *i*- $\text{C}_4\text{H}_9\text{Cl}$, 0.05 g (0.4 mmol) of C_8H_{18} (2 isomers), and 0.21 g (1.4 mmol) of $\text{C}_{11}\text{H}_{16}$ (6 isomers; Friedel-Crafts reaction products⁴⁶). No gas was evolved upon protolysis of the toluene solution. In an analogously performed control experiment using commercial Mg powder (50 mesh, 0.3 mm) under the same reaction conditions (2 h, 70°C, toluene) no reaction at all with *i*- $\text{C}_4\text{H}_9\text{Cl}$ was observed.

Entry 2: The experiment was performed with 0.91 g of Mg^* (Table 2, entry 10; 35.3 mmol) and 3.17 g (34.3 mmol) of *i*- $\text{C}_4\text{H}_9\text{Cl}$ in 100 ml of *n*-heptane analogously to that in toluene. After filtration of the reaction mixture 1.71 g of a solid with the composition C 35.2, H 5.8, Mg 23.8, Cl 35.0% was obtained. Protolysis of 390.8 mg of the solid produced 55.0 ml of gas (20°C/1 bar) with 65.5% *i*- C_4H_{10} and 34.5% H_2 (MS analysis). From the amount of *i*- C_4H_{10} evolved a yield of 37.6% of isobutylmagnesium chloride (with respect to the converted *i*- $\text{C}_4\text{H}_9\text{Cl}$, below) was calculated. GC-MS coupling analysis of the *n*-heptane solution after protolysis was used to identify and quantify 1.50 g (16.2 mmol) of *i*- $\text{C}_4\text{H}_9\text{Cl}$ and 0.06 g (0.5 mmol) of C_8H_{18} (2 isomers). After the evaporation of the solution to dryness in vacuo the residue was hydrolyzed, and 1.40 mmol of isobutane was evolved. Complexometric titration showed that 0.70 mmol Mg^{2+} was present, corresponding to a yield of 7.7% of diisobutylmagnesium.

Entry 3: To Mg^* prepared by thermal decomposition of 4.20 g (10.0 mmol) of **4** in vacuo (10^{-2} mbar) at 230°C for 0.5 h was added 0.735 g (5.0 mmol) of *p*- $\text{C}_6\text{H}_4\text{Cl}_2$ and then THF (10 ml). The resulting slurry was stirred while the temperature was thermostated at 25°C. After reaction times of 20 and 60 min small aliquots of the solution were removed, decomposed by $\text{C}_2\text{H}_5\text{OH}$, and analyzed for *p*- $\text{C}_6\text{H}_4\text{Cl}_2$, $\text{C}_6\text{H}_5\text{Cl}$, and C_6H_6 by gas chromatography. The results are presented in Table 10.

2 from Mg^* and THF: A suspension of 2.43 g of Mg^* freshly prepared from MgH_2 (Table 2, entry 1; 96 mmol) in 75 ml of THF was heated to reflux for 10 d. At predetermined time intervals 2.0-ml samples of the solution were removed and protolyzed by using toluene/ CH_3OH (50:1) containing an analytically weighed amount of *n*- C_8H_{18} as a standard, and the amount of *n*-butanol produced was analyzed by gas chromatography. Dependence of the percentage of *n*-butanol (with respect to Mg) on the reaction time (in h): 11.4% (51), 19.6% (99), 25.4% (243). An analogous experiment was performed using 1.60 g (62 mmol) of Mg^* freshly prepared from **4** (procedure e) and 100 ml of THF. Dependence of the percentage of *n*-butanol (with respect to Mg) on the reaction time (in h): 3.5% (5), 10.7% (20), 19.3% (52), 23.7% (96).

Isolation and Characterization of 2: A suspension of 2.69 g of Mg^* generated from MgH_2 (Table 2, entry 1; 106 mmol) in 50 ml of THF was heated at reflux for 30 d. The unreacted magnesium was filtered off, washed with THF, and the filtrate evaporated to dryness in vacuo (0.2 mbar) leaving 3.00 g of **2** as a grey powder.



Calcd. C 54.40 H 9.13 Cl 0.00 Mg 18.35 Ti 0.00

Found C 50.00 H 8.80 Cl 3.92 Mg 17.83 Ti 0.28

Protolysis of 82.3 mg of **2** yielded 16.1 mg of THF and 33.6 mg of *n*-butanol; THF/*n*- $\text{C}_4\text{H}_9\text{OH}$ = 0.50:1.00. — IR (nujol): $\tilde{\nu}$ = 1100, 1029, 885, 565, 530 cm^{-1} . — ^1H NMR ($[\text{D}_8]\text{THF}$): δ = -0.32 (t, J = 6.7 Hz; $-\text{CH}_2\text{CH}_2\text{Mg}-$), 1.27–2.21 (m; $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 3.49–4.16 (m; $-\text{CH}_2\text{CH}_2\text{O}$). — ^{13}C NMR ($[\text{D}_8]\text{THF}$): δ = 9.81 (t, J = 106 Hz; C-3), 26.37 (t, J = 147 Hz; THF, C-3,4), 30.50 (t, J = 121 Hz; C-4), 39.48 (t, J = 122 Hz; C-5), 67.37 (t, J = 136 Hz; C-6), 68.37 (t, J = 131 Hz; THF, C-2,5); further signals of low intensity at δ = 14.60, 20.35, 31.15, 35.53, and 63.77 were also observed.

1-(Trimethylsilyl)-4-(trimethylsilyloxy)butane from 2 and Trimethylsilyl Chloride (TMS): A suspension of 2.43 g of Mg^* generated from MgH_2 (Table 2, entry 1; 96 mmol) in 75 ml THF was heated under reflux for 8 h, and then the unreacted magnesium was removed by filtration. After the addition of 5.43 g (50 mmol) of TMS the filtrate was heated at reflux for 16 h. The solvent and the

excess TMS were removed by evaporation in vacuo (14 mbar), and the residual liquid was distilled in vacuo to give 3.92 g of (18%) 1-(trimethylsilyl)-4-(trimethylsilyloxy)butane (b.p. 83–85°C/14 mbar). — ¹H NMR (CDCl₃, 400 MHz): δ = -0.05 (s; 9H), 0.08 (s; 9H), 0.47 (m; 2H), 1.32 (m; 2H), 1.52 (m; 2H), 3.55 (t; 2H).

4-Benzoylbutyl Benzoate from 2 and Benzoyl Chloride: The experiment was performed in the same way and by use of the same amount of starting materials as described above for the reaction with TMS. After the addition of 50 mmol of benzoyl chloride, the mixture was heated to reflux for 0.5 h, and THF and excess benzoyl chloride were removed in vacuo (14 mbar). The residual liquid was treated with ice/water, extracted with ether, and the ether layer evaporated in vacuo. The residual oil was distilled in vacuo to give 3.95 g (14%) of 4-benzoylbutyl benzoate (b.p. 80–85°C/10⁻² mbar). — IR (film): $\tilde{\nu}$ = 1733, 1695 cm⁻¹. — ¹H NMR (CDCl₃, 400 MHz): δ = 1.88 (m; 4H), 3.02 (m; 2H), 4.33 (m; 2H), 7.2–7.7 (m; 6H), 7.8–8.2 (m; 4H).

Reaction of Mg* with Hydrogen at 240°C/1 bar: 0.4–0.7-g samples of the particular Mg* were placed into the glass vessel of the thermovolumetric apparatus⁴⁴⁾.

The vessel was evacuated, filled with hydrogen at normal pressure, and connected to an automatically recording gas buret⁴⁴⁾, which was also filled with hydrogen. The sample was heated to 240°C (5 min) and then maintained at this temperature until the hydrogenation had been completed. The time dependence of hydrogen uptake for different Mg* samples is represented in Figure 2.

CAS Registry Numbers

1 R = *i*Bu, X = Cl: 5674-02-2 / 1 R = *s*Bu, X = Cl: 15366-08-2 / 1 R = *t*Bu, X = Cl: 677-22-5 / 1 R = *neo*-C₈H₁₇, X = Cl: 13132-23-5 / 1 R = H₂C=C(CH₃)CH₂, X = Cl: 5674-01-1 / 1 R = C₆H₅, X = Cl: 100-59-4 / 1 R = 1-naphthyl, X = Cl: 90767-34-3 / 1 R = *n*Bu, X = Cl: 693-04-9 / 1 R = *t*Bu, X = Cl: 2259-30-5 / 1 R = (Z)-MeCH=CH, X = Br: 13154-14-8 / 1 R = (E)-MeCH=CH, X = Br: 13154-15-9 / 1 R = 2-(3-cyclohexenyl)ethyl, X = Cl: 126755-02-0 / 1 R = 3-(2-methylenecyclopropyl)propyl, X = Cl: 126755-03-1 / 1 R = 6-(tetrahydro-2-pyranyloxy)hexyl, X = Cl: 69049-76-9 / 1 R = cycloheptyl, X = Br: 78378-12-8 / 1 R = ClMg[CH₂]₄, X = Cl: 22758-42-5 / 1 R = HC≡CCH₂, X = Cl: 65032-28-2 / 1 R = *p*-ClC₆H₄, X = Cl: 51833-36-4 / 1 R = *p*-ClMgC₆H₄, X = Cl: 51833-37-5 / 2: 65168-80-1 / 3: 120-12-7 / 4: 86901-19-1 / TMS: 75-77-4 / MgH₂: 7693-27-8 / *n*BuCl: 109-69-3 / *i*BuCl: 513-36-0 / *t*BuCl: 507-20-0 / *s*BuCl: 78-86-4 / *t*BuBr: 507-19-7 / *neo*-C₈H₁₇Cl: 753-89-9 / (Z)-MeCH=CHBr: 590-13-6 / (E)-MeCH=CHBr: 590-15-8 / Cl[CH₂]₄Cl: 110-56-5 / HC≡CCH₂Cl: 624-65-7 / C₆H₅Cl: 108-90-7 / H₂C=C(CH₃)CH₂Cl: 563-47-3 / Mg: 7439-95-4 / 1-chloro-6-(tetrahydro-2-pyranyloxy)hexane: 2009-84-9 / 1-chloro-2-(3-cyclohexenyl)ethane: 63540-001 / 1-chloro-3-(2-methylenecyclopropyl)propane: 126755-04-2 / cycloheptyl bromide: 2404-35-5 / 1-chloronaphthalene: 90-13-1 / *p*-dichlorobenzene: 106-46-7 / 1-(trimethylsilyl)-4-trimethylsilyloxybutane: 7140-91-2 / 4-benzoylbutyl benzoate: 65411-93-0 / benzoyl chloride: 98-88-4

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