Tetrahydrofuran-Soluble Magnesium Dihydride by Catalytic Hydrogenation of Magnesium☆)

Borislav Bogdanović*, **Peter Bons**, **Manfred Schwickardi**, and **Klaus Seevogel**

Max-Planck-Institut für Kohlenforschung,
W-4330 Mülheim a.d. Ruhr, FRG

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Upon hydrogenation of magnesium in THF using homogeneous magnesium-anthracene transition-metal halide catalysts in the presence of small amounts of $MgCl_2$ and solubilizing agents L, a dissolved form of magnesium hydride (MgH_2') is produced. The preferred L's are quinuclidine (QC) or organomagnesium compounds; however, organoaluminium and -boron compounds can also be used. The fraction n of magnesium hydride produced in the dissolved form and the stability of the MgH_2' solutions are investigated as a function of the kind and the amount of solubilizing agents and catalysts. The optimized method for the preparation of MgH_2' is described. The magnesium hydride dissolved in THF is characterized by IR spectroscopy. In order to elucidate the role of the solubilizing agents, THF-soluble $MgCl_2$-containing stoichiometric $MgH_2 \cdot$ QC model complexes are also prepared and characterized by IR spectra. Advantages and disadvantages of using MgH_2' for synthetic purposes instead of catalytically prepared suspensions of magnesium hydride (MgH_2^*) are discussed.

Magnesium dihydride (in the following designated as magnesium hydride), prepared by non-catalytic[1] or catalytic[2] routes, is a solid, insoluble in all common inert organic solvents[1,3].

Ashby et al. have first prepared THF-soluble magnesium hydrides of the HMgX type (X being an alkyl or aryl[4], dialkyl or arylamido[5], alkoxy or aryloxy[3b,6] group or Cl, Br[3a]) by reaction of active forms of magnesium hydride[7] with MgX_2 in THF in a 1:1 molar ratio.

Attempts to prepare THF solutions of hydridomagnesium chloride (HMgCl) by reaction of catalytically prepared MgH_2[2] (in the following designated as MgH_2^*) with $MgCl_2$ in THF have been of moderate success[8]. THF solutions of HMgCl can, however, be prepared in nearly quantitative yields by catalytic hydrogenation of magnesium in $MgCl_2$-saturated THF at 0°C. By concentrating these HMgCl solutions or by catalytic hydrogenation of magnesium in a $MgCl_2$ suspension in THF, hydridomagnesium chloride solutions having a H^-/Cl^- ratio > 1 but not higher than 3 (corresponding to the formula $MgH_2 \cdot HMgCl$) can be obtained[8].

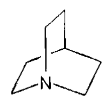
Preparation of THF Solutions of Magnesium Hydride

In continuation of our investigations on the catalytic hydrogenation of magnesium, we have found that upon hydrogenation of magnesium in THF using homogeneous magnesium-anthrancene transition-metal halide catalysts[2a–c] in the presence of non-stoichiometric amounts of $MgCl_2$[2d–f] and of *additional* solubilizing agents (L), the resulting magnesium hydride is produced partially or almost completely in a dissolved form[9]. [In the following, as in eq. (1), the dissolved magnesium hydride is designated as MgH_2'.] The preferential additional solubilizing agents L are quinuclidine (QC) or organomagnesium compounds; however, organoaluminium and organoboron compounds can also be used.

$$\mathrm{Mg} + p\,\mathrm{MgCl_2} + q\,\mathrm{L} + \mathrm{H_2} \xrightarrow{\text{cat. / THF}^{2)}} \underbrace{[(\mathrm{MgH_2})_n,\ (\mathrm{MgCl_2})_p,\ \mathrm{L}_q,\ \mathrm{Cat.}]^{10)}}_{\mathrm{MgH_2'}\ \text{solution in THF}}$$

$$0 \le p \le 0.15 \qquad\qquad + (1-n)\ \mathrm{MgH_2^*}\downarrow$$

$$0 \le q \le 0.30$$



QC

This report emphasizes the preparation and characterization of the THF-solubilized magnesium hydride. Its application as a reagent for organic or inorganic syntheses has already been described[11,12] or will be described separately. The most important advantages of using MgH_2' solutions instead of MgH_2^* suspensions in THF or solid MgH_2^*[2] for synthetic purposes are as follows:

– MgH_2' solutions display, in general, a higher reactivity and/or their application affords higher yields in chemical reactions; in some cases, reaction products differing from those when MgH_2^* is used are obtained; these statements hold particularly for the application of MgH_2' solutions in the synthesis of metal[12] and element hydrides, intermetallic compounds, and their hydrides and carbides[13];

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– more accurate dosing of magnesium hydride, since the concentration of the solution can be exactly determined;

– safer and easier handling, since MgH_2' solutions (which can be up to 5 molar) do not ignite in the air as does MgH_2^* suspended in THF or as a solid[2].

The disadvantages of MgH_2' solutions with respect to suspended or solid MgH_2^* are the ubiquitous solubilizing agents and catalysts in the solution, which can interfere with a desired synthesis, and their relative low stability at ambient temperature (see next section).

As demonstrated in numerous experiments (Tables 1 – 3), the fraction of magnesium hydride produced in a dissolved state, *n*, depends on both the kind and the amount of solubilizing agents and catalyst applied. The percentage of dissolved magnesium hydride (experiments 1.1, 1.2, 1.6, 1.8, 1.10, and 1.15 ≡ experiments 1, 2, 6, 8, 10, and 15 of Table 1) increases when transition-metal chlorides (MCl_z) of the series

$$TiCl_4 < MnCl_2 < CrCl_3 < FeCl_2$$

are used for the preparation of the catalyst. In further optimization experiments, therefore, only the Cr or Fe catalyst have been employed.

If either of the two solubilizing agents $MgCl_2$ or QC is omitted (exp. 1.3 and 1.4), at best only a negligible amount of MgH_2' is produced. Hence, the presence of both components is indispensable. With increasing concentrations of $MgCl_2$ and QC (Cr catalyst, exp. 1.5 to 1.7[14]; Fe catalyst, exp. 1.9 to 1.13) the percentage of MgH_2' increases (rapidly at low and slowly at higher concentrations).

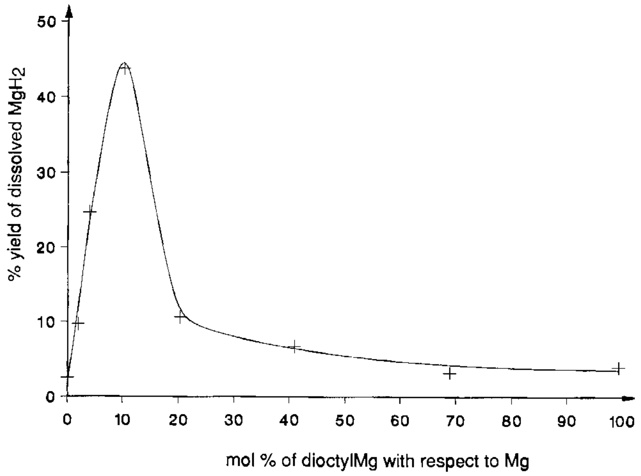


Figure 1. Dependence of MgH_2' yield on the amount of dioctMg used as a solubilizing agent. The experiments were carried out at 18 – 25°C and 60 – 80 bar H_2 pressure by using 4.9 g of Mg powder, 1 mol-% of MgA – $CrCl_3$, 3.6 mol-% of $MgCl_2$, and variable amounts of dioctMg in 200 ml of THF

The yield of MgH_2' at relatively low QC level (4.8 to 5.0 mol-%) can be further improved by increasing the amount of the Fe catalyst[15] from 1 to 10 mol-% (exp. 1.10, 1.14, and 1.15). (This effect remains weak when the Cr catalyst is used, exp. 1.6 and 1.8). With 10 mol-% of $FeCl_2$ (exp. 1.15) after hydrogenation a MgH_2' solution free of MgH_2^* is obtained.

In view of the minimization of the amount of the catalyst and the solubilizing agent (but without achieving the maximum stability of solutions, see next section), the MgH_2' solutions with QC and $MgCl_2$ as solubilizing agents are routinely prepared in our laboratory according to exp. 1.10 (standard experiment, described in detail in the experimental part).

In place of $MgCl_2$ and QC as solubilizing agents Grignard compounds (exp. 2.1 to 2.4, 2.9, and Table 3) or diorganomagnesium compounds in the presence (exp. 2.6 – 2.8 and 2.11) or absence of $MgCl_2$ (exp. 2.5 and 2.10) can be applied.

Surprisingly, with both the Cr and Fe catalyst, the increase of the octylmagnesium chloride (octMgCl) (exp. 2.2 to 2.4, 3.2, 3.4, and 3.5) or dioctylmagnesium (dioctMg) concentration (exp. 2.6 to 2.8) does not lead to an increase but to a small decrease in *n*. In a series of experiments analogous to 2.6-2.8 but with a higher amount of THF (ca. five times) this effect is clearly demonstrated (Figure 1). By increasing the amount of dioctMg in these hydrogenation experiments from 0 to 100 mol-% (with respect to Mg) the yield of MgH_2' showed a pronounced maximum of ≈ 45% between 10 and 15 mol-% of dioctMg. At or near equimolar ratios of dioctMg versus Mg, the yield of MgH_2' amounts to only 5% or less.

The use of organomagnesium compounds with ether functional groups[2c,16] (exp. 2.9 and 2.10) has brought apparently little or no advantage with respect to the yield of MgH_2' over alkylmagnesium compounds (exp. 2.4 and 2.5). Triorganoaluminium or -boron compounds in combination with $MgCl_2$ (exp. 2.12 to 2.14) have been found to be less effective as solubilizing agents than organomagnesium compounds. Organomagnesium as well as organoaluminium compounds with longer alkyl chains (exp. 2.3 and 2.13) are more efficient solubilizing agents than those with shorter alkyl chains (exp. 2.1 and 2.12). Among the Grignard compounds investigated, the best results are achieved with octMgCl (which can be generated in situ, exp. 2.4) in combination with the Fe catalyst (Table 3). In these experiments the increase of the amount of $FeCl_2$ from 0.6 up to 4 mol-% at constant concentration of octMgCl (5 mol-%; exp. 3.1, 3.2, and 3.6) results in an increase of the MgH_2' yield from 53 to 88%. A typical procedure for the preparation of a MgH_2' solution in the presence of octMgCl (exp. 3.2) is described in the experimental part.

Stability of MgH_2' Solutions

MgH_2' solutions separated from MgH_2^* by centrifugation and stored at room temperature show more or less rapid precipitation of magnesium hydride. Simultaneously with this precipitation, the MgH_2' solutions become more and more viscous with time and finally solidify (THF polymerization). However, MgH_2' solutions prepared with trioctylaluminium or tribenzylboron as solubilizing agents (exp. 2.13 and 2.14) are stable at room temperature, i.e. they do not show MgH_2 precipitation and maintain a low viscosity

Table 1. Preparation of MgH'_2 solutions using different catalysts (MCl_z) and variable amounts of $MgCl_2$ and QC as solubilizing agents. Hydrogenations were carried out at 18–25°C and 60–80 bar H_2 pressure by using 10.0 g of Mg powder and 1 mol-% of anthracene in 70–100 ml of THF

No. of exp.	MCl_z (mol-%)[a]	$MgCl_2$ mol-%[a]	QC or QC·HCl[14] (mol-%)[a]	duration of hydr. [h]	$\frac{[mol\ H^-]}{l}$	fraction of MgH'_2[%] (100 n)	$MgH_2\cdot(MgCl_2)_{p/n}(QC)_{q/n}$ p/n[b]	q/n	data referring to the stability of MgH'_2 solutions at room temp.[c]
1	$TiCl_4$ (1)	–	QC·HCl (9.8)	22	3.1	38	0.13	0.26	
2	$MnCl_2$ (1)	3.6	QC (5.0)	10	5.6	51	0.07	0.10	
3	$CrCl_3$ (1)	4	–	$3\frac{1}{4}$	0.7	6	0.65	–	
4	$CrCl_3$ (1)	–	QC (21)	24	0.0	0	–		
5	$CrCl_3$ (1)	–	QC·HCl (1.3)	4	4.7	58	0.01	0.02	
6	$CrCl_3$ (1)	–	QC·HCl (4.4)		5.4	69	0.03	0.07	Fig. 2, —*—[d]
7	$CrCl_3$ (2)	–	QC·HCl (17)	20	5.7	83	0.11	0.23	
8	$CrCl_3$ (10)	3.4	QC (4.8)		7.0	78	0.05	0.07	
9	$FeCl_2$ (1)	3.4	QC (2.7)		8.3	66	0.05	0.04	Fig. 2, —Δ—[e]
10[f]	$FeCl_2$ (1)	3.6	QC (5.0)	4	8.0	75	0.05	0.07	Fig. 2, —▼—[g]
11	$FeCl_2$ (1)	15[h]	QC (5.0)		6.3	76	0.20	0.07	
12	$FeCl_2$ (1)	3.6	QC (20)	3	7.8	79	0.05	0,26	
13	$FeCl_2$ (1)	10	QC (20)		6.9	88	0.12	0.22	
14	$FeCl_2$ (4)	3.4	QC (4.8)		9.7	87	0.04	0.06	
15	$FeCl_2$ (10)	3.4	QC (4.8)		9.3	96	0.04	0.06	

[a] With respect to the amount of Mg powder used. — [b] In the calculation of the p/n number the amount of $MgCl_2$ formed by the reaction of MCl_z with Mg is neglected. — [c] Unless otherwise stated. — [d] After 4.5 h at reflux temperature, the hydride content of the solution decreased by 30%. — [e] Stability of the MgH'_2 solution at room temp. upon addition of 5 mol-%[a] of trioctylaluminium (see text). — [f] Standard experiment. — [g] The solution was stored at −25°C for 2 months without changes in the hydride ion content. — [h] $MgCl_2$ partly suspended.

at room temperature for a longer period of time (see text below).

If MgH'_2 solutions are diluted with the same volume of ether, pentane, or toluene, magnesium hydride immediately and irreversibly precipitates. This precipitation as well as the unsuccessful attempts to prepare MgH'_2 solutions by *subsequent* addition of $MgCl_2$ and QC or HMgCl and QC to the catalytically prepared MgH^*_2 suspensions in THF[2] (see Experimental) indicate that MgH'_2 solutions in THF are metastable like solutions of AlH_3 in ether and THF[17].

The stability of MgH'_2 solutions at room temperature, prepared according to eq. (1) and separated from MgH^*_2 by centrifugation, is investigated as a function of the kind and amount of solubilizing agents and catalyst. For this purpose, MgH'_2 solutions are kept at room temperature, and after a definite period of time samples are taken from solutions, centrifuged, and their hydride content is analyzed. These results are included in Tables 1-3 and illustrated in Figure 2.

The MgH'_2 solutions prepared by using $MgCl_2$ and QC as the solubilizing agents (exp. 1.6 and 1.10; Figure 2: —*—, Cr catalyst; —▼—, Fe catalyst) are, in general, of low stability. (The stability of these solutions can, however, be improved by addition of trioctylaluminium, see text below.)

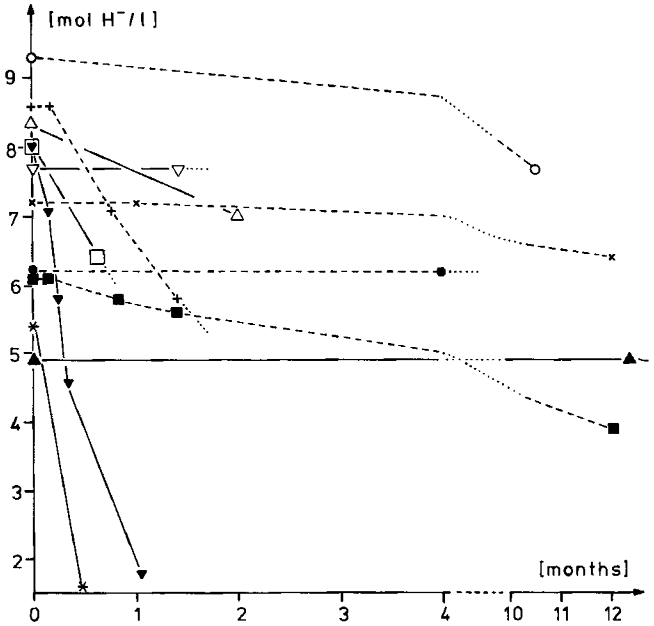


Figure 2. Decrease of MgH'_2 concentration in THF at room temperature with time: – –○– –, exp. 3.6; – –+– –, exp. 3.2; – –×– –, exp. 3.5; – –●– –, exp. 3.3; – –■– –, exp. 3.4; – –Δ– –, exp. 1.9 upon addition of 5 mol-% of trioctylaluminium; ——□——, exp. 2.7; ——▼——, exp. 1.10; ——▽——, exp. 2.8; ——*——, exp. 1.6; ——▲——, exp. 2.13

Table 2. Preparation of MgH'_2 solutions using the magnesium anthracene–$CrCl_3$ catalyst (1 mol-%)[a] and $MgCl_2$ and/or different organometallics (L) as solubilizing agents. Hydrogenations were carried out at 18–25°C and 60–80 bar H_2 pressure by using 10.0 g of Mg powder in ≈70 ml of THF

No. of exp.	$MgCl_2$ mol-%[a]	L (mol-%)[a]	duration of hydr. [h]	$\frac{[\text{mol H}^-]}{\text{l}}$	fraction of MgH'_2 [%] (100n)	$MgH_2\cdot(MgCl_2)_{p/n}\cdot L_{q/n}$ p/n[b]	q/n	data referring to the stability of MgH'_2 solutions at room temp.[c]
1	–	buMgCl (4.4)	$4\frac{1}{4}$	4.9	43	–	0.10	8d: solid.
2	–	octMgCl (2.2)	$5\frac{1}{3}$	7.5	68	–	0.03	9d: solid.
3	–	octMgCl (4.4)	$4\frac{1}{2}$	7.2	66	–	0.07	35d: solid.[d]
4	–	octCl[e] (12.7)	$6\frac{1}{2}$	6.0	57	–	0.25	35d: solid.
5	–	dioctMg (6.0)	$3\frac{3}{4}$	6.5	61	–	0.10	2d: solid.
6	3.6	dioctMg (3.0)	6	8.0	75	0.05	0.04	21d: solid.
7	3.6	dioctMg (6.0)		8.0	76	0.05	0.08	Fig. 2, —□—; 28d: solid.
8	3.6	dioctMg (11)	6	7.7	69	0.05	0.17	Fig. 2, —▽—; 2 m: solid.
9	–	$Cl(CH_2)_3CH_3$[e] (6.0)	$5\frac{2}{3}$	7.5	75	–	0.09	
10	–	$[MeO(CH_2)_4]_2Mg$[2c,16] (6.0)	$7\frac{1}{2}$	6.3	58	–	0.10	10d: solid.
11	3.6	$(PhCH_2)_2Mg$ (6.0)	$2\frac{1}{2}$	7.2	63	0.06	0.10	21d: solid.
12	3.6	bu_3Al (6.0)	$3\frac{1}{2}$	2.7	24	0.15	0.25	2m: unchanged; 18m: decreased by 82%
13[f]	4	oct_3Al (6.0)	$7\frac{1}{2}$	4.9	48	0.08	0.13	19m: unchanged; Fig. 2, —▲—
14	3.6	$(PhCH_2)_3B$ (6.0)	7	3.5	30	0.12	0.20	19m: unchanged

[a] With respect to the amount of Mg powder used. — [b] In the calculation of the *p*/*n* number the amount of $MgCl_2$ formed by the reaction of $CrCl_3$ with Mg is neglected. — [c] Unless otherwise stated; m = month; solid. = the solution solidified after the given time; unchanged = no change in the hydride content of the solution. — [d] The solution was stored at –25°C for 2 m without changes in the hydride content. — [e] The Grignard compound was prepared in situ from the halide and Mg powder. — [f] Using the $FeCl_3$ instead of the $CrCl_3$ catalyst, we obtained the same result.

These solutions should, therefore, be stored at temperatures ≤ –25°C. At such temperatures a solution, prepared according to the standard experiment (exp. 1.10), can be stored for two months without undergoing changes in the hydride content.

The stability of the MgH'_2 solutions at room temperature prepared by using $MgCl_2$ and dioctMg (Cr catalyst, exp. 2.6 to 8; Figure 2: –□– and –▽–) or octMgCl as solubilizing agent (Fe catalyst, exp. 3.2, 3.4 and 3.5; Figure 2: – – – lines) increases strongly with increasing amounts of organomagnesium compound. Only minor changes in the hydride content of the solutions over a course of several months have been observed (Figure 2: – – ■ – – and – – × – –). In experiment 3.3, in which $MgCl_2$ (7.2 mol-%) in addition to octMgCl is applied, the resulting MgH_2' solution remains unchanged during a period of four months at room temperature (Figure 2: – – ● – –). By increasing the amount of the Fe catalyst from 1 up to 4 mol-%, a MgH'_2 solution is obtained (exp. 3.6; Figure 2: – – ○ – –) whose hydride content at room temperature is lowered by only 17% within 10.5 months. For the time being, this result represents both with respect to the stability and yield (88%) an optimum for the MgH'_2 preparation.

Surprisingly, the MgH'_2 solutions prepared by using $MgCl_2$ and trioctylaluminium (exp. 2.13; Figure 2: – ▲ –) or tribenzylboron (exp. 2.14) as solubilizing agents and kept at room temperature, have revealed no changes in the hydride content during a period of 19 months. Unfortunately, the yield of MgH'_2 in these cases is rather low (48 and 30%). We have, therefore, attempted to improve the stability *and* the yield of MgH'_2 solutions by hydrogenating Mg powder in the presence of $MgCl_2$, trioctylaluminium and QC. An experiment performed in the same way as experiment 1.9, but with 5 mol-% of trioctylaluminium, yields still only 48% of MgH'_2. In a further experiment, in which 5 mol-% of trioctylaluminium (with respect to MgH'_2) is *subsequently* added to a MgH'_2 solution prepared according to exp. 1.9, the MgH'_2 solution shows a marked increase in stability

Table 3. Preparation of MgH_2' solutions using variable amounts of the $FeCl_2$ catalyst and octMgCl as a solubilizing agent. Hydrogenations were carried out at 18–25°C and 60–80 bar H_2 pressure by using 10.0 g of Mg powder and 1 mol-%[a] of anthracene in ≈70 ml of THF

No. of exp.	$FeCl_2$ mol-%[a]	$MgCl_2$ mol-%[a]	octMgCl mol-%[a]	duration of hydr. [h]	$\frac{[\text{mol H}^-]}{1}$	fraction of MgH_2' [%] (100 n)	$MgH_2\cdot(MgCl_2)_{p/n}\cdot L_{q/n}$		data referring to stability of MgH_2' solutions at room temp.[c]
							p/n[b]	q/n	
1	0.6	–	5	9	5.7	53	–	0.10	14d: solid.
2	1	–	5	4	8.6	82	–	0.06	Fig. 2, — + —; 2m: solid.
3	1	7.2	5		6.2	61	0.12	0.08	Fig. 2, —●—; 6m: solid.
4	1	–	15		6.1	57	–	0.26	Fig. 2, —□—
5	1	–	30		7.2	58	–	0.52	Fig. 2, — x —
6	4	–	5	4	9.3	88	–	0.06	Fig. 2, — o —

[a] With respect to the amount of Mg powder used. — [b] See footnote [b] of Table 2. — [c] m = month; solid. = the solution solidified after the given time.

(– △ – of Figure 2). Thus, a comparison of the lines – ▼ – and – △ – in Figure 2 reveals that the stability of MgH_2' solutions prepared by use of QC as a solubilizing agent can be markedly improved by subsequent addition of trioctylaluminium.

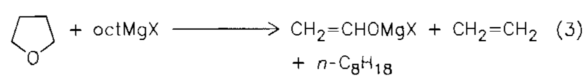
Spectroscopic and Chemical Characterization of the Dissolved Magnesium Hydride

In the ^1H-NMR spectra of the HMgX compounds (X = alkyl, aryl[4], dialkyl- or arylamido[18], alkoxy, aryloxy[6]) in THF, a Mg–H signal is not observed.

The ^1H-NMR spectra of MgH_2' in $[D_8]$THF (prepared both in the presence of QC · HCl (according to exp. 1.6) and dioctMg and $MgCl_2$ (according to exp. 2.8)[19]) do not reveal any signal either which might be assigned to a hydridic proton. In the ^1H-NMR spectrum of the MgH_2' solution prepared in the presence of dioctMg and $MgCl_2$, the intensities of the signals of the CH_3 group and of the C-3 to C-7 methylene protons are too high in comparison with those of the C-1 and C-2 protons in the same spectrum, indicating the presence of *n*-octane in addition to octylmagnesium compounds in the solution. In the distillate obtained by evaporation of this $[D_8]$THF solution in vacuo, the presence of *n*-octane (≈ 20% of the octyl groups of the dioctMg used) has been confirmed by gas chromatography. In a similar experiment (exp. 3.5) only 2-3% of *n*-octane resulting from octMgCl are found in the solution after hydrogenation. The hydrogenation[20] [eq. (2)] and/or the reaction of octylmagnesium compounds with $[D_8]$THF[21] [eq. (3)] but also residual H_2O in $[D_8]$THF can be taken into account for the formation of *n*-octane in these solutions.

Also, in the ^{13}C-NMR spectrum of the above mentioned MgH_2' solution (measured at – 80°C) the signals of the octyl groups are superimposed by those of *n*-octane. Of particular interest are the signals at δ = 9.1 and ≈ 9.6 (weak signal) as well as those at δ = 40.6 and 41.5 (weak signal), which can be assigned to the C-1 and C-3 atoms of Mg–octyl groups, respectively; this signal pattern indicates the presence of two different Mg–octyl moieties in the solution. On the basis of a comparison with the ^{13}C-NMR spectra of an authentic dioctMg sample (C-1: δ = 9.2; C-3: δ = 40.7) and a 1:0.9 mixture of dioctMg with $MgCl_2$ (C-1: δ = 9.2 and 9.7; C-3: δ = 40.7 and 41.5) in $[D_8]$THF, measured under the same conditions, the signals at δ = 9.1 and 40.6 and at ≈ 9.6 and 41.5 in the ^{13}C-NMR spectrum of MgH_2' can be tentatively assigned to dioctMg and octMgCl, respectively. The ^{13}C-NMR spectrum thus provides no evidence of the presence of Mg–octyl species in the investigated MgH_2' solution other than dioctMg and octMgCl.

$$\text{dioctMg} + 2\ H_2 \xrightarrow{\text{cat. / THF}} MgH_2 + 2\ n\text{-}C_8H_{18} \qquad (2)$$



(3)

The IR spectra of the solid or matrix-isolated magnesium hydride[22] can serve as references for the IR spectrum of the dissolved magnesium hydride.

The IR spectrum of catalytically prepared[2] solid magnesium hydride (Figure 3)[23] reveals large ranges of absorption at 1300–900 and 700–500 cm^{-1}, obviously, consisting of several unresolved broad bands. These bands are associated with stretching and bending modes of hydride bridges of the structurally ill-defined polymeric $(MgH_2)_x$ species. These spectral features are in marked contrast to those of matrix-isolated monomeric MgH_2, which shows two sharp, well assigned bands at 1550 and 420 cm^{-1} [22b]. (Only an insignificant difference is noted between the IR spectra of catalytically prepared solid magnesium hydride[23] and solid magnesium hydride reported earlier[22a]).

In the IR spectrum of a centrifuged MgH_2' solution (≈ 1 M in MgH_2'; exp. 1.6; Figure 4b) the spectral features arising from MgH_2' are partly obscured by THF absorption. They are more apparent in the difference spectrum (Figure 4c), which shows a broad absorption due to the Mg—H stretching modes in the frequency range of 1300—1000 cm^{-1}, similar to that found for solid magnesium hydride (see Figure 3). A second band, assignable to a Mg—H—Mg bending mode, is centered at 670 cm^{-1}. This band is narrower and somewhat shifted to higher wave numbers, in comparison with that observed for solid MgH_2. Thus, in the IR spectra of the dissolved MgH_2 only absorption bands assignable to bridging hydrogens are detectable. The intensity of the bands is concentration-dependent.

To confirm the assignment of Mg—H vibrations, the IR spectrum of MgD_2', prepared in the same manner as MgH_2' (exp. 1.6), has been recorded. The corresponding stretching and bending modes in MgD_2' are shifted to the range of 1000—700 and to 495 cm^{-1}, respectively.

In order to determine the role of the solubilizing agent QC, a MgH_2' solution which has been prepared with 17 mol-% of QC · HCl (exp. 1.7) is evaporated to dryness under vacuum at room temperature. Only a small fraction (9.6%) of the QC used in the synthesis is sublimed off and can subsequently be detected in the distillate. When, thereafter, the distillation residue is hydrolyzed and again subjected to distillation under vacuum, 93% of the residual QC is found in the distillate. This result indicates that the QC is chemically complexed in the $MgH_2(MgCl_2)_{0.11}(QC)_{0.23}$ solution of exp. 1.7. In order to increase the concentration of the complexed QC, a large amount of QC (MgH_2' : QC = 1:2) is added to the above solution and stirred at room temperature for several days. No further reaction of the additional QC with the MgH_2' solution takes place, since the additional QC can be completely sublimed off by the evaporation of the solution under vacuo. These experiments suggest that QC forms a complex during the catalytic hydrogenation of magnesium in THF in the presence of $MgCl_2$ and QC[14]. The complexation of QC can occur with the MgH_2 in statu nascendi and/or with $MgCl_2$. It can be assumed that due to this process, the precipitation of MgH_2 from the solution is (partly) prevented.

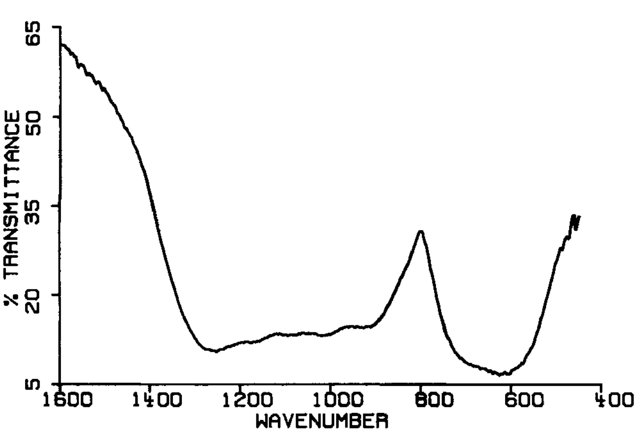


Figure 3. IR spectrum (KBr) of catalytically prepared[2] solid magnesium hydride[23]

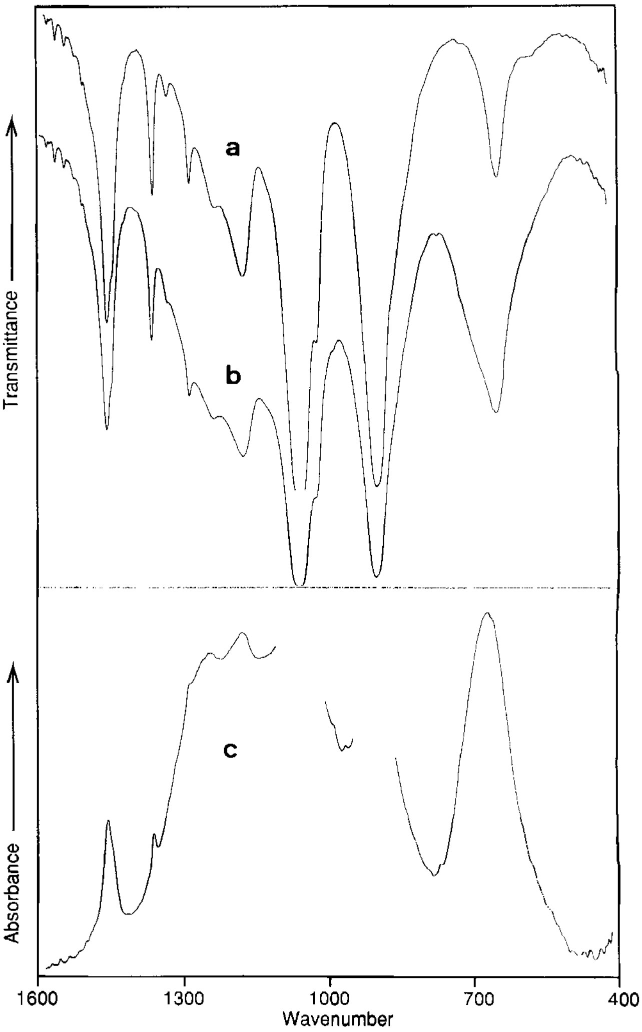


Figure 4. IR transmission spectra of a centrifuged MgH_2'/THF solution in the presence of the hydrogenation catalyst (**b**) and the hydrogenation catalyst in THF (**a**) (equivalent concentration as in **b**). The difference spectrum, (**b**) — (**a**), given in the absorbance scale (**c**) (fragmentary in the frequency region of strong THF absorptions)

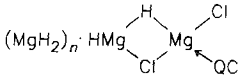
In this context, experiments have been undertaken to prepare definite *stoichiometric* soluble MgH_2—QC complexes as model complexes for dissolved MgH_2. As already mentioned above, such complexes *cannot* be obtained by reaction of QC with MgH_2' solutions. Therefore, catalytic hydrogenations of magnesium in the presence of larger amounts of QC and catalytic amounts of $MgCl_2$ (Table 4), are carried out.

Attempts to catalytically hydrogenate Mg powder in THF in the presence of 40—50 mol-% of QC and small amounts[14] of (exp. 4.1) $MgCl_2$ or in the absence of the latter have failed; almost no absorption of hydrogen takes place. (Larger amounts of QC seem to inhibit the activity of the Cr hydrogenation catalyst.) If the amount of QC is lowered to 20 mol-% (exp. 4.2) slow hydrogenation of Mg occurs. When the hydrogenation is interrupted at a Mg conversion of 58%, a solution of the composition $MgH_2 \cdot (MgCl_2)_{0.13} \cdot (QC)_{0.24}$ (based on the determination of complexed QC, see Experimental) can be obtained. If, because of the low catalyst activity, both the catalyst and the $MgCl_2$ concentration are increased and the hydrogenation is interrupted at a Mg conversion of 48%, a MgH_2^*-free solution of the composition $MgH_2 \cdot (MgCl_2)_{0.37}$(complexed QC)$_{0.92}$ (exp. 4.3) is obtained which, after standing at room temperature for one week, shows no decrease in the hydride content. The IR spectrum of this solution (Figure 5, top) displays the same range of Mg – H stretching vibrations and the Mg – H – Mg deformational vibration at 670 cm^{-1} as the MgH_2' solution prepared by use of smaller amounts of QC and $MgCl_2$ (Figure 4b, c; exp. 1.6). In the IR spectrum of the corresponding deuterated solution (Figure 5, bottom; exp. 4.4) the Mg – D stretching and deformational vibrations appear at 1000 – 700 and 495 cm^{-1}, respectively.

Upon evaporation of the solution of experiment 4.3 to dryness, a solid of the composition $MgH_2 \cdot (MgCl_2)_{0.37} \cdot (QC)_{0.92} \cdot (THF)_{0.14}$ is obtained, which is nearly completely soluble in THF but scarcely soluble in toluene and insoluble in ether. Attempts to remove $MgCl_2$ from the solution by addition of 1,4-dioxane have failed, since MgH_2 precipitates together with the $MgCl_2$ – 1,4-dioxane adduct.

According to the same method, attempts have been made to prepare a soluble MgH_2 – QC complex with a ≈ 1:2 molar ratio of the components. By catalytic hydrogenation of Mg powder in the presence of 60 mol-% of QC and 2.8 mol-% of $MgCl_2$ and interruption of the hydrogenation at a Mg conversion of 21 %, a THF solution can be obtained which upon evaporation to dryness affords a solid of the composition $MgH_2(MgCl_2)_{0.43}$(complexed QC)$_{2.25}$ (exp. 4.5). The solid is soluble in toluene (≈1 M with respect to MgH_2). The IR spectrum of the THF solution of the solid shows no changes in the position of Mg – H vibrations with respect to those of Figure 4b, c and Figure 5, top, and also in this case the addition of 1,4-dioxane to the THF solution results in coprecipitation of MgH_2 and $MgCl_2$ – 1,4-dioxane.

On the basis of the composition of model complexes of the dissolved MgH_2 (exp. 4.3 and 4.5) it appears that $MgCl_2$ and QC, but not THF, are associated with MgH_2 in the THF-soluble MgH_2 – $MgCl_2$ – QC-complexes. The composition of the model complexes is in agreement with the experimental results that $MgCl_2$ and QC are both indispensable for the preparation of MgH_2' solutions (exp. 1.3 and 1.4) and that removal of $MgCl_2$ from these solutions by the addition of 1,4-dioxane causes precipitation of MgH_2. These facts together with the experimentally observed formation of $MgCl_2$ – QC (1:2) complexes in THF suggest that actually "dissolved MgH_2" may be composed of MgH_2 aggregates associated with $MgCl_2$ by chlorine and/or hydrogen bridges with $MgCl_2$ simultaneously complexed with QC:



Since the amount of complexed QC in experiment 4.5 (and probably also in experiment 1.12) exceeds by far that of $MgCl_2$, in this case the possibility of the complexation of QC by the dissolved MgH_2 should also be taken into account.

Table 4. Preparation of MgH_2 – $MgCl_2$ – QC complexes by catalytic hydrogenation of Mg powder (0.20 mol) in the presence of $MgCl_2$ and QC (or QC and QC · HCl) at 18 – 25°C and 60 – 80 bar H_2 in 50 – 60 ml of THF

No. of exp.	MgA–$CrCl_3$ mol%[a]	$MgCl_2$ mol%[a]	QC and QC·HCl (mol%[a])	duration of hydr. [h]	conversion [%]	MgH_2:$MgCl_2$[b]:QC[c] in solution
1	2	–	QC (56) QC·HCl (4.6)	68	3	
2	2	4.7	QC (20)	20	58	1.0:0.13:0.24
3[d]	4	7	QC (49) QC·HCl (8.8)	6	48	1.0:0.37:0.92
4[e]	4	9.3	QC (57)	11	41	1.0:0.37
5[d]	4	2.8	QC (58)	16	21	1.0:0.43:2.25

[a] With respect to the amount of Mg powder used. — [b] Calculated on the basis of the sum of $MgCl_2$ + $CrCl_3$ + QC · HCl. — [c] Complexed QC, see Experimental. — [d] The experiments were repeated several times and afforded the same results. — [e] Deuteration experiment.

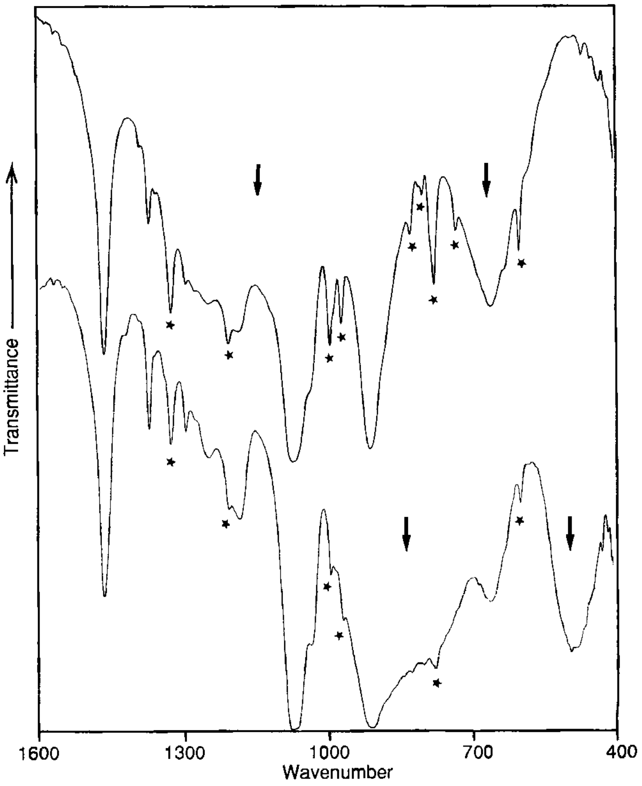


Figure 5. Top: IR spectrum of $MgH_2 \cdot (MgCl_2)_{0.37} \cdot (QC)_{0.92}$ (exp. 4.3) in THF. Bottom: IR spectrum of the corresponding MgD_2 solution (exp. 4.4). Both solutions are ≈1 M with respect to MgH_2 or MgD_2. Absorptions arising from MgH_2 and MgD_2 in the spectra are marked by arrows; peaks denoted by stars are due to QC vibrations

On the other hand, the importance of THF as solvent for MgH$_2$ should not be ignored, since, as mentioned above, magnesium hydride is immediately precipitated by the addition of extraneous solvents to MgH$_2'$ solutions.

The authors thank Dr. *R. Mynott* and his coworkers for measurements and discussions concerning NMR spectra and Dr. *L. Aleandri* for useful comments.

Experimental

^{1}H NMR: Bruker WH-400, Bruker AM-200. – ^{13}C NMR: Bruker WM-300. – IR: Nicolet 7199 FT/IR spectrometer.

All reactions and operations were carried out under argon in air- and water-free solvents. THF was heated at reflux over MgEt$_2$ or magnesium–anthracene (MgA) and distilled. Mg powder (Eckart Werke PK 31, 270 mesh) and anthracene (99%, Rütgerswerke AG) were used without further purification. H$_2$: 99.9%, Messer Griesheim. The saturated solution of anhydrous MgCl$_2$ in THF ($\approx$ 0.5 M) was prepared by reaction of Mg powder with 1,2-dichloroethane in THF as described for the preparation of MgBr$_2$[24] · QC and QC · HCl were commercial products.

All the experiments conducted to improve the preparation of MgH$_2'$ (Tables 1–3) are performed by using 10 g (ca. 0.4 mol) of Mg powder in 70–100 ml of THF; hydrogenation is carried out at room temp. (18–25°C) at an initial hydrogen pressure ranging between 60 and 80 bar. In most cases, a quantitative conversion of Mg to MgH$_2'$ occurs. The hydrogenation in the temperature range between 18 and 25°C seems to be quite optimal for the preparation of MgH$_2'$. In an experiment, performed under the same conditions as experiment 3.2 but at a hydrogenation temperature of 0°C, the hydrogenation rate becomes impracticably low (9 and 23% of MgH$_2'$ after 18 and 36 h, respectively). Furthermore, no dissolved magnesium hydride is produced in experiments carried out parallel to the experiments 1.6 and 3.2 but at an elevated hydrogenation temperature ranging between 45 and 65°C.

The dissolved fraction of magnesium hydride [n in eq. (1)] in the experiments is determined by centrifuging aliquots of the suspensions prepared according to eq. (1) (1 h at 10000 rpm) and analyzing by mass spectrometry the hydrogen evolved upon alcoholysis of MgH$_2^*$-free solutions. The compositions of the MgH$_2'$ solutions, neglecting the catalyst, given in the Tables 1–3, [MgH$_2$ · (MgCl$_2$)$_{p/n}$ · (L)$_{q/n}$], are calculated on the assumption that the solubilizing agents do not coprecipitate with MgH$_2^*$. This assumption has been experimentally verified in experiment 1.10 (the standard experiment), whereby 97% of Cl$^-$ ions and 98.5% of QC are found in the solution (see below).

Preparation of a MgH$_2'$ Solution Using MgCl$_2$ and QC as Solubilizing Agents (exp. 1.10; standard experiment): A 250-ml cylindrical two-necked flask served as the reaction vessel and glass insert for a 500-ml high-grade steel autoclave with a flat bottom[25]. The flask was equipped with a three-way tap, a stopper, and a magnetic stirring bar. 10.00 g (411 mmol) of Mg powder (270 mesh) and 0.73 g (4.1 mmol) of anthracene were placed into the flask, the flask was evacuated, filled with argon, and 30 ml of THF was added. The suspension, after addition of 4–5 drops of EtBr, was stirred at room temp. for 2 h until the formation of the orange precipitate of MgA[2f,26] was completed. Upon cooling (water 15°C) and stirring, 0.56 g (4.4 mmol) of anhydrous FeCl$_2$ (exothermic reaction, color change to dark brown!), 11.0 ml of a 1.86 M QC solution in THF (20.5 mmol), and 30 ml of a 0.49 M MgCl$_2$ solution in THF (14.7 mmol) were subsequently added to the reaction mixture. The glass vessel was inserted into the 500-ml autoclave and with intensive magnetic stirring at 20–25°C (inner temperature![25]) the mixture was hydrogenated at an initial hydrogen pressure of 60 bar. After $\approx$4 h the hydrogen pressure dropped to $\approx$ 40 bar and then remained constant (cf. Figure 6). The autoclave was depressurized, opened, the content of the glass vessel was siphoned out into a graduated Schlenk tube and the glass vessel rinsed with a small amount of THF. 15.0 ml of the total volume of 78 ml of the turbid deeply colored MgH$_2'$ solution was centrifuged at 10000 rpm[27] for 1 h and 2.0 ml of the clear supernatant solution protolyzed by the addition of C$_2$H$_5$OH (cooling with water!) to give 398 ml of gas (20°C, 1 bar) of the composition (MS analysis): H$_2$ 95.9%, C$_2$H$_5$OH 2.0%, THF 2.1%. From the amount of hydrogen evolved, the concentration of the MgH$_2'$ solution was calculated to be of 4.0 M and the yield of MgH$_2'$ 75% (with respect to the Mg powder used). 2.0 ml of the centrifuged solution was hydrolyzed with H$_2$O and 5 N HNO$_3$, and the Cl$^-$ content of the aqueous solution was determined according to the method of Volhard using a 0.1 N AgNO$_3$ solution. The Cl$^-$ content of the aqueous solution was found to be 97% of the sum of Cl$^-$ contents of MgCl$_2$ and FeCl$_2$ used for the experiment. 10.0 ml of the centrifuged solution was hydrolyzed with C$_2$H$_5$OH/H$_2$O/conc. NaOH, the mixture was evaporated in vacuo to dryness and the residue dried at 10^{-5} bar for 2 h. In the distillate was found by acidimetric titration (0.1 N HCl) 98.5% of QC used in the experiment. On the basis of the MgH$_2'$ yield and the amounts of MgCl$_2$ and QC used in the experiment, the composition of the MgH$_2'$ solution as MgH$_2$ · (MgCl$_2$)$_{0.05}$ · (QC)$_{0.07}$ (Table 1) could be calculated.

Preparation of a MgH$_2'$ Solution Using octMgCl as a Solubilizing Agent (exp. 3.2): The experiment and analysis were performed in the same way as described above, except that instead of MgCl$_2$ and QC solutions a 1.74 M octMgCl solution in THF (11.8 ml, 20.5 mmol) was used as the solubilizing agent. The hydrogen uptake during hydrogenation of Mg with time in this experiment is shown in Figure 6.

Also, all the other experiments of Tables 1–3 were performed analogously.

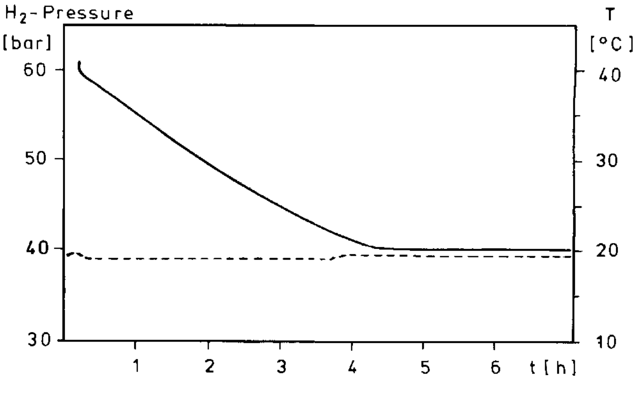


Figure 6. Dependence of the hydrogen uptake on time during hydrogenation of Mg (exp. 3.2); ——, hydrogen pressure; – – –, hydrogenation temperature

Attempts to Dissolve the MgH$_2^*$ Suspended in THF by Treatment with MgCl$_2$ and QC or HMgCl and QC: 2.04 g (18.3 mmol) of QC and 18 ml of a 0.48 M MgCl$_2$ solution in THF (8.6 mmol) were added to a suspension of 82 mmol of MgH$_2^*$ in 20 ml of THF prepared by catalytic hydrogenation of Mg using the Cr catalyst[2a] (MgH$_2^*$: MgCl$_2$: QC = 1 : 0.22 : 0.10). The suspension was stirred at room temp. for 3 d. Thereafter, a 2.0-ml sample of the centrifuged solution was subjected to alcoholysis to yield 5 ml of gas, corresponding to a dissolution of MgH$_2^*$ of maximally 2.5%.

6.39 g (57.5 mmol) of QC was added to a suspension of 170 mmol of MgH_2^* in 40 ml of THF, prepared as described above, and the suspension was stirred at room temp. for 4 h. Thereafter, a 2.0-ml sample of the centrifuged solution was converted into 0.2 ml of gas by alcoholysis. To the rest of the suspension was added 10 ml of a 1.13 M HMgCl solution in THF[8], and the suspension was stirred at room temp. for an additional 18 h. After that time, a 2.0-ml sample of the centrifuged solution was subjected to alcoholysis to yield 8.6 ml of gas, corresponding to the amount of HMgCl added to the solution. After heating the suspension at reflux for another 18 h, no dissolution of MgH_2^* was detectable.

Preparation of a MgH_2' Solution in [D_8]THF Using QC · HCl and ^{1}H-NMR Spectrum thereof: The preparation was carried out according to the experiment 1.6. 1.99 g (82 mmol) of Mg powder was hydrogenated in 8.5 ml of [D_8]THF in the presence of 1 mol-% of the $CrCl_3-MgA$ catalyst and 6.6 mol-% of QC · HCl at room temp. for 18 h. The yield of MgH_2' was 55%; the solution was 5.3 M with respect to MgH_2'. The ^{1}H-NMR (400 MHz) spectra of the solution as well as of the solution diluted with [D_8]THF to twice its volume did not reveal any signals in the range of $\delta = -47$ to $+12.5$.

Preparation of a MgH_2' Solution in [D_8]THF Using dioctMg and $MgCl_2$ and NMR Spectra thereof: The preparation was carried out according to experiment 2.8. 2.50 g (103 mmol) of Mg powder was hydrogenated in 18 ml of [D_8]THF in the presence of 2 mol-% of the $CrCl_3-MgA$ catalyst, 9.5 mol-% of dioctMg, and 5 mol-% of $MgCl_2$ at room temp. for 19 h. The yield of MgH_2' was 28%; the solution was 1.3 M with respect to MgH_2'. The ^{1}H-NMR spectrum was measured in the range of $\delta = -18.9$ to $+13$ at $+20$ and $-80\,^\circ$C. – ^{1}H NMR (200 MHz, 20 °C): $\delta = -0.70$ (t, 2H, $MgCH_2$), 0.84 (t, 5H, CH_3), 1.21 (m, 14H, $-[CH_2]_5-$), 1.46 (m, 2H, $MgCH_2CH_2$). – ^{13}C NMR (75.5 MHz, $-80\,^\circ$C): $\delta = 9.1$ (t, $J = 105$ Hz) and ≈ 9.6 (C-1), 15.0 (q, $J = 124$ Hz, C-8), 24.0, 24.1 (t, $J = 126$ Hz, C-7), 31.0, 31.6, 31.9, 33.3, 33.7 (t, $J = 125-128$ Hz, C-2, C-4 to -6), 36.7 (anthracene), 40.6 (t, $J = 122$ Hz) and 41.5 (C-3).

Preparation of Comparison Solutions of (a) dioctMg and (b) dioctMg and $MgCl_2$ in [D_8]THF and ^{13}C-NMR Spectra thereof

a) 0.25 g of dioctMg was dissolved in 7.0 ml of [D_8]THF, the solution was stirred and filtrated at $-78\,^\circ$C. The saturated solution kept at $-78\,^\circ$C was used for the measurement of the ^{13}C-NMR spectrum.

b) 0.21 g (2.2 mmol) of $MgCl_2$ and 0.62 g (2.5 mmol) of dioctMg were dissolved in 8.0 ml of [D_8]THF. The solution was centrifuged and the clear supernatant layer was used for recording the ^{13}C-NMR spectrum. Both spectra were measured at 75.5 MHz and $-80\,^\circ$C; the pertinent ^{13}C-NMR data are given in the general part of this paper.

Determination of the Free (a) and of the Complexed QC (b) in a MgH_2' Solution Prepared by Use of QC · HCl as a Solubilizing Agent

a) 5.0 ml of a centrifuged MgH_2' solution prepared according to the experiment 1.7 (5.7 mol H^-/l) containing 3.22 mmol of QC (based on the amount of QC · HCl used) was evaporated to dryness in vacuo, and the distillation residue was dried at room temp. and 0.1 mbar for 4 h. The distillate contained 0.31 mmol of QC as determined by acidimetric titration (0.1 N HCl) that is 9.6% of the amount of QC · HCl used in the experiment.

b) The distillation residue was suspended in 3–4 ml of toluene and 5 ml of C_2H_5OH; then 5 ml of conc. NaOH was added to the mixture with stirring. After repeated distillation of the volatile components under vacuum and drying of the residue at room temp. at 0.1 mbar for 2 h, 2.70 mmol (84% of the QC · HCl amount used in the experiment) of the complexed QC was analyzed in the distillate by acidimetric titration as described above and identified as such by GC-MS coupling analysis. (For the determination of total QC in a MgH_2' solution see standard experiment.)

Attempted Reaction of QC with a MgH_2' Solution: 7.10 g (63.9 mmol) of QC in 10 ml of THF was added to 11.5 ml of the centrifuged MgH_2' solution prepared according to experiment 1.7 (5.7 mol H^-/l; MgH_2:QC = 1:2). The solution was then stirred at room temp. After stirring for 1, 2, and 24 d, 4.0-ml samples were taken from the solution, and the amount of free QC was determined (as described above) to be 94, 88, and 100% of the amount of QC added. From this experiment it can be concluded that a MgH_2' solution does not react with free QC.

Preparation and Analysis of the Solution of a Solid with the Composition $MgH_2 \cdot (MgCl_2)_{0.37} \cdot (QC)_{0.92}$ (exp. 4.3): Experiment and analysis were carried out in an analogous way as the in standard process (1.10), but hydrogenation was interrupted after 6 h and a pressure drop of ≈10 bar. The volume of the solution after hydrogenation was 72.5 ml. Alcoholysis of 2.0 ml of the centrifuged solution afforded 129 ml of H_2 (20 °C, 1 bar) of 97.6% purity from which a yield of 48% of dissolved MgH_2 (with respect to the Mg powder used) and a hydride ion concentration of 2.62 mol/*l* is calculated. The total amount of dissolved Mg in the solution (sum of MgH_2' + $MgCl_2$) was found to be 118.7 mmol, as determined by hydrolysis of a 1.0-ml sample of the centrifuged solution and complexometric titration of Mg^{2+} with a 0.1 M Titriplex III solution.

The determination of the free and complexed QC in the solution was conducted as described above. The amounts of the free and complexed QC in the solution were found to be 30.0 and 87.6 mmol, respectively; the total amount (117.6 mmol) was in good agreement with the sum of QC and QC · HCl (119.4 mmol) used in the experiment. From the amount of hydrogen evolved on alcoholysis, the total amount of $MgCl_2$, QC · HCl, and $CrCl_3$ used in the experiment, and the amount of complexed QC in the solution, the composition of the solution was computed to be $MgH_2 \cdot (MgCl_2)_{0.37} \cdot (QC)_{0.92}$ (Table 4).

For the determination of THF 9.5 ml of the centrifuged solution (2.62 mol H^-/l; = 12.4 mmol of dissolved MgH_2) was evaporated to dryness under vacuum and the resulting solid dried at 20 °C for 2.5 h under high vacuum. The solid was suspended in 15 ml of toluene, then 10 ml of EtOH and ≈1 ml of H_2O were added and the volatile components of the mixture distilled at 20–60 °C/0.1 mbar into a trap cooled with liquid nitrogen. In the distillate 125.0 mg (1.73 mmol) of THF was analyzed by gas chromatography by using *n*-octane as internal standard (MgH_2:THF = 1.0:0.14).

Another 13.5 ml of the centrifuged solution (= 17.7 mmol of dissolved MgH_2) was evaporated and dried under vacuum in the same way as described above to afford 3.25 g of a solid [calculated for 17.7 mmol of a solid of the composition $MgH_2 \cdot (MgCl_2)_{0.37} \cdot (QC)_{0.92}$ 2.90 g]. 1.00 g of the solid was stirred at 20 °C in 50 ml of THF for 1.5 h and the suspension was subsequently centrifuged (1 h; 10000 rpm). Alcoholysis of 2.0 ml of the clear supernatant solution afforded 89.0 ml (20 °C, 1 bar) of H_2 of 96.1% purity, corresponding to 1.78 mol H^-/l. The solid was thus quite soluble in THF. 1.11 g of the solid was stirred in 5.0 ml of toluene at 20 °C for 1.5 h and then the suspension centrifuged. The concentration of H^- in the centrifuged toluene solution (determined as described above) was found to be 0.2 mol/*l*. Application of the same procedure revealed that the solid was insoluble in ether.

Preparation and Analysis of the Solution of a Solid with the Composition $MgH_2 \cdot (MgCl_2)_{0.43} \cdot (QC)_{2.25}$ (exp. 4.5): Experiment and analysis were carried out in an analogous way as the standard experiment (exp. 1.10), but the hydrogenation was interrupted after 16 h and a pressure drop of $\approx$ 9 bar. The volume of the solution after hydrogenation was 73.0 ml. Alcoholysis of 2.0 ml of the centrifuged solution furnished 59.4 ml of H_2 (20°C, 1 bar) of 97.8% purity from which a yield of 21% of dissolved MgH_2 (with respect to the Mg powder used) and a hydride ion concentration of 1.21 mol/*l* is calculated. The determination of the free and complexed QC in the solution was carried out as described on p. 1049. The amounts of the free and complexed QC were found to be 20.5 and 99.6 mmol, respectively; their total amount (120.1 mmol) was in good agreement with the amount of QC (119.4 mmol) used in the experiment. From the amount of hydrogen evolved upon alcoholysis, the total sum of the $MgCl_2$ and $CrCl_3$ used in the experiment, and the amount of complexed QC in the solution the composition of the solution can be described as $MgH_2 \cdot (MgCl_2)_{0.43} \cdot (QC)_{2.25}$ (Table 4).

The determination of THF in the solid obtained by evaporation of the solution to dryness and of the solubility of the solid in toluene was carried out as described in the experiment 4.3 (MgH_2:THF = 1.0:0.27). After evaporation of 15.0 ml of the solution (1.21 mol H^-/*l*; 9.1 mmol of dissolved MgH_2) to dryness 2.89 g of a solid [calculated for 9.1 mmol of the solid $MgH_2 \cdot (MgCl_2)_{0.43} \cdot (QC)_{2.25} \cdot (THF)_{0.27}$ 3.06 g] was obtained. The solubility of the solid in toluene was found to be 1.05 mol H^-/*l*.

After the addition of 1.0 ml of 1,4-dioxane to 10.0 ml of the solution (12.1 mol of dissolved MgH_2), the mixture was stirred at room temp. for 3 h and subsequently centrifuged. The H^- concentration of the supernatant solution was found to be 0.45 mol/*l*.

CAS Registry Numbers

QC: 100-76-5 / Mg: 7439-95-4 / MgH_2: 7693-27-8 / $MgCl_2$: 7786-30-3 / QC · HCl: 39896-06-5 / $TiCl_4$: 7550-45-0 / $MnCl_2$: 7773-01-5 / $CrCl_3$: 10025-73-7 / $FeCl_2$: 7758-94-3 / buMgCl: 693-04-9 / octMgCl: 38841-98-4 / dioctMg: 24219-37-2 / $ClMg(CH_2)_3CH_3$: 693-04-9 / $[MeO(CH_2)_4]_2Mg$: 108023-48-9 / $(PhCH_2)_2Mg$: 6928-77-4 / bu_3Al: 1116-70-7 / oct_3Al: 1070-00-4 / $(PhCH_2)_3B$: 1694-84-4 / anthracene: 120-12-7

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[*] Dedicated to Professor *Paul Binger* on the occasion of his 60th birthday.

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[371/90]