Diorganomagnesium Compounds from Magnesium, Hydrogen, and 1-Alkenes and Their Application in Synthesis

Borislav Bogdanović*, Peter Bons[+], Stanimir Konstantinović[++], Manfred Schwickardi, and Uwe Westeppe[+++]

Max-Planck-Institut für Kohlenforschung,
Kaiser-Wilhelm-Platz-1, D-4330 Mülheim an der Ruhr, FRG

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1-Alkenes are converted in high yields to the corresponding primary diorganomagnesium compounds by transition metal-catalyzed hydromagnesation reaction using catalytically prepared suspended (MgH_2^*) or dissolved magnesium hydride (MgH_2'). The most active hydromagnesation catalysts have been found to be combinations of zirconium tetrahalides with MgH_2^* or MgH_2'. The reaction is highly regio- and chemoselective. The diorganomagnesium compounds prepared in situ from magnesium, hydrogen, and 1-alkenes can be applied to the synthesis of organic and organometallic compounds just as Grignard compounds (Scheme 3, reactions 3−11). Dioctylmagnesium undergoes the growth reaction with ethene in the presence of quinuclidine and is oxidized by molecular oxygen in high yield to 1-octanol.

Dialkylmagnesium compounds are usually prepared by disproportionation[1] or alkylation[1c,2] of Grignard compounds. The Cp_2TiCl_2-catalyzed addition of an active form of magnesium hydride to 1-alkenes has been reported by Ashby et al.[3] Grignard compounds can be prepared from 1-alkenes, conjugated dienes or alkynes by transition metal-catalyzed exchange with alkyl-Grignard reagents having β-hydrogen(s) (hydromagnesation reaction)[4].

Several years ago we described a direct "one-pot" synthesis of dialkylmagnesium compounds from magnesium, hydrogen, and 1-alkenes by the catalytic hydrogenation of magnesium to magnesium hydride[5] (in the following designated as MgH_2^*) followed by the in situ addition of the latter to 1-alkenes in the presence of homogeneous transition metal catalysts[6] (Scheme 3). The transition metal-catalyzed addition of MgH_2^* to conjugated dienes, α-unsaturated ethers, and amines has been applied to the preparation of allylic, benzylic[7], and intramolecularly coordinated diorganomagnesium compounds[5c,8], respectively. Moreover, it has been recently discovered that a tetrahydrofuran-soluble forms of catalytic magnesium hydride[9] (in the following designated as MgH_2') can also be utilized as a reagent for the hydromagnesation of 1-alkenes[10] (see below).

In the first part of this paper we summarize our findings concerning the preparation of dialkylmagnesium compounds from magnesium, hydrogen and 1-alkenes. In the second part the application of the in situ prepared or, in a few cases, of pure isolated dialkylmagnesium compounds to organic and organometallic syntheses[11] is described.

Preparation of Diorganomagnesium Compounds from Magnesium, Hydrogen, and 1-Alkenes

The homogeneous catalysts used for the hydrogenation of magnesium to MgH_2^* are usually prepared by the reaction of magnesium anthracene · 3 THF (MgA) with $CrCl_3$ or $TiCl_4$ in the presence of an excess of magnesium in THF[5]. These THF-soluble systems (in the following designated as MgA–$CrCl_3$ or –$TiCl_4$ catalysts) catalyze the addition of MgH_2^* to lower 1-alkenes, ethene, propene, and even 1-butene[6,13]. The MgA–$TiCl_4$ catalyst is more active than the MgA–$CrCl_3$ catalyst (Experiment 1.1 versus Experiment 1.3, Experimental part). Thus, dipropylmagnesium is prepared in high yields by hydrogenation of magnesium with the help of the MgA–$TiCl_4$ catalyst at 20−25°C and subsequent reaction of the resulting MgH_2^* suspension with propene[14] at 85°C employing the same catalyst (Experiments 2.1 and 2.2).

The activity of MgA–$CrCl_3$ or –$TiCl_4$ catalysts for the hydrogenation of magnesium is strongly enhanced when small amounts of $MgCl_2$ (7−8 mol-% related to Mg) are utilized as a cocatalyst[6c,15]. The time needed to quantitatively hydrogenate a sample of Mg powder to MgH_2^* can thus reduced by a factor of ten (e.g. from 20−24 to 2−2.5 h). The cocatalytic effect of $MgCl_2$ has been utilized for the preparation of diethyl- and dibutylmagnesium, butylethylmagnesium, and dioctylmagnesium (Experiments 1.3, 3.2, 4.2 and Table 5, respectively). The addition of MgH_2^*, obtained by hydrogenation of Mg powder with the aid of the MgA–$TiCl_4$ catalyst and $MgCl_2$ cocatalyst, to ethene or 1-butene is again accomplished without requiring an additional hydromagnesation catalyst.

More active catalysts for the hydromagnesation of 1-alkenes than those discussed above have been found to be

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[+] Current address: Metallgesellschaft AG, Frankfurt am Main.
[++] Current address: Faculty of Science, University of Kragujevac, 34000 Kragujevac, Yugoslavia.
[+++] Current address: BAYER AG, Krefeld-Uerdingen.

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combinations of MgH_2^* (or MgH_2'[9,10]) with zirconium tetrahalides[6]. These catalysts can be used for the hydromagnesation of both lower and higher 1-alkenes. The following "standard" procedure has proved to be successful for the synthesis of diethyl-, dipropyl-, dibutyl-, butylethyl-, dioctyl-, and dipentadecylmagnesium (in the following: Et_2Mg, Pr_2Mg, Bu_2Mg, EtBuMg, Oct_2Mg, and $Pentadec_2Mg$): magnesium is first hydrogenated at 20–25°C with the aid of the MgA–$CrCl_3$ catalyst affording a MgH_2^* suspension in THF which displays a particularly high reactivity (see below); after the addition of a catalytic amount of $ZrCl_4$ (1–2 mol-%) to the suspension, the mixture is allowed to react with the respective 1-alkene at elevated temperature (70–90°C) (Experiments 1.2, 2.4, 3.1, 4.1, Oct_2Mg-standardized experiment, and $Pentadec_2Mg$). *The reaction of MgH_2^* with ethene (Experiment 1.2) or with ethene and 1-butene (Experiment 4.1) in the presence of the MgH_2^*–$ZrCl_4$ catalyst is very vigorous and exothermic, so that precautions must be taken for the reaction temperature never to exceed ~100°C; at temperatures ⩾160–170°C serious explosions can occur due to reaction of MgH_2^* with THF.* The preparation of Et_2Mg from MgH_2^* and ethene catalyzed with $ZrCl_4$ can also be performed in ether (Experiment 1.4).

Hydrogenation of higher 1-alkenes, e.g. 1-octene, can be carried out appropriately under normal pressure in refluxing THF/1-alkene mixtures. The progress of the reaction can be monitored by taking samples out of boiling mixtures and determining their content of *dissolved* magnesium (see Experimental, preparation of Oct_2Mg). The influence of various hydromagnesation catalysts and of the way of preparing MgH_2^* suspension on the rate of MgH_2^*-to-1-octene addition has been investigated by this method (Figures 1 and 2).

In the first series of experiments, magnesium is hydrogenated with the help of the MgA–$CrCl_3$ catalyst (20–25°C/80–90 bar H_2), and the resulting MgH_2^* suspension is treated with 1-octene at reflux temperature by employing various transition metal compounds (1 mol-%) as hydromagnesation catalysts (Figure 1). As can be seen in Figure 1, the best results are achieved with MgH_2^*–ZrX_4 (X = Cl, Br, I) catalysts, among which the MgH_2^*–ZrI_4 catalyst appears to be the most efficient one. In the series of transition metal chlorides $TiCl_4$, $ZrCl_4$, and $HfCl_4$ the rate of hydromagnesation decreases in the order Zr > Ti > Hf. Cp_2TiCl_2[3,4c] in combination with MgH_2^* exhibits a low catalytic activity. In the control experiment of this series (Figure 1, –△–) no transition metal compound is added after the hydrogenation step. The experiment indicates that the MgA–$CrCl_3$ catalyst has a negligible activity towards the MgH_2^*-to-1-octene addition after it has been used as a hydrogenation catalyst.

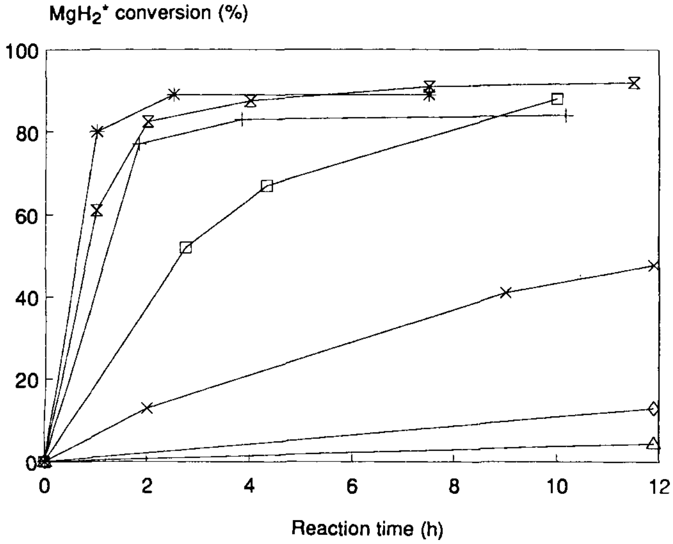


Figure 1. Time dependence of the addition of MgH_2^* to 1-octene in boiling THF/1-octene for various hydromagnesation catalysts; MgH_2^* suspension prepared at 20–25°C with the aid of the Cr catalyst. MgH_2^* : 1-octene : catalyst = 100 : 230 : 1; –∗–, ZrI_4; –⪻–, $ZrCl_4$ (standardized experiment); –+–, $ZrBr_4$; –□–, $TiCl_4$; –×–, $HfCl_4$; –◇–, Cp_2TiCl_2; –△–, no catalyst added

In the second series of experiments the method of preparing MgH_2^* suspensions has been varied, whereas in all of these experiments $ZrCl_4$ (1 mol-%; reflux temperature) has been used as a hydromagnesation catalyst (Figure 2). The MgH_2^* suspension of highest activity in this comparison results from the hydrogenation of magnesium with the help of the MgA–$CrCl_3$ catalyst at 20–25°C (Figure 2, –⪻–, "standardized experiment"). MgH_2^* suspensions of slightly lower activity for the hydromagnesation of 1-octene in the presence of the Zr catalyst are obtained when hydrogenations of magnesium are carried out with the MgA–$CrCl_3$ catalyst at 60°C, with the MgA–$TiCl_4$ catalyst at 20–25°C, or with the same catalysts in the presence of $MgCl_2$ as a cocatalyst (Figure 2 and Experiments 5.1 and 5.2). When $MgCl_2$ is employed as a cocatalyst, the hydromagnesation of 1-octene can be improved by increasing the amount of the Zr catalyst (Experiment 5.3), while an increase in the reaction temperature only causes a minor increase in the reaction rate (Experiment 5.4). A sample of MgH_2^* produced

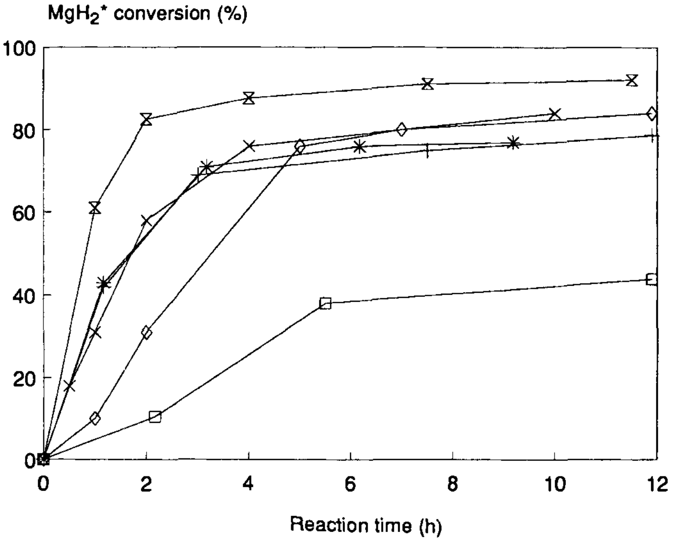


Figure 2. Time dependence of the addition of MgH_2^* to 1-octene in boiling THF/1-octene for MgH_2^* suspensions prepared with the aid of various catalysts and at various temperatures; $ZrCl_4$ was used as hydromagnesation catalyst; MgH_2^* : 1-octene : $ZrCl_4$ = 100 : 230 : 1; –⪻–, Cr catalyst, 20–25°C (standardized experiment); –∗–, Ti catalyst, 20–25°C; –+–, Cr catalyst, 60°C; –×–, Ti catalyst, $MgCl_2$ cocatalyst, 60°C; –◇–, Cr catalyst, $MgCl_2$ cocatalyst, 25°C; –□–, Cr catalyst, 60°C, MgH_2^* separated from the catalyst solution and dried in vacuum

with the use of the MgA–$CrCl_3$ catalyst at 60 °C is separated from the catalyst solution and dried in vacuum. The activity of this sample for hydromagnesation of 1-octene in the presence of the Zr catalyst has proved to be low (Figure 2, –□–).

The course of the addition of the solubilized magnesium hydride[9] (MgH_2') to 1-decene using 1 mol-% of $ZrCl_4$ as a hydromagnesation catalyst in a boiling THF/1-decene mixture is represented in Figure 3 (see also Table 6, Experimental). With Oct_2Mg as a solubilizing agent for MgH_2'[9], a higher addition rate is observed when an excess of 1-decene with respect to MgH_2' is used for the addition (15%; –△–) than when an excess of MgH_2' with respect to 1-decene is applied for the same (15%; –+–). In the presence of an excess of MgH_2' (15%), comparable results are achieved if Oct_2Mg (–+–) or quinuclidine (–□–) are applied as solubilizing agents for MgH_2'[10].

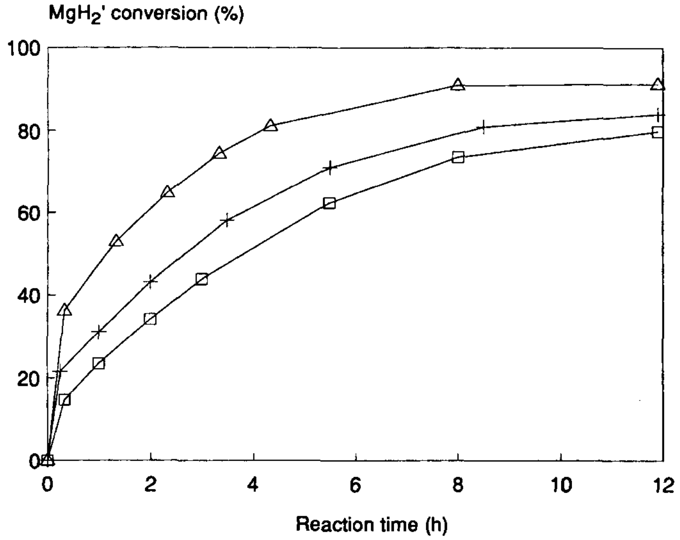
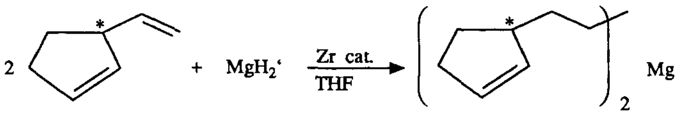


Figure 3. Time dependence of the addition of MgH_2' to 1-decene in boiling THF/1-decene; –△–, 1-decene in excess of Oct_2Mg-solubilized MgH_2'; –+–, Oct_2Mg-solubilized MgH_2' in excess of 1-decene; –□– quinuclidine-solubilized MgH_2' in excess of 1-decene

Hydromagnesation of the optically active 3-vinyl-1-cyclopentene via MgH_2' affording bis[2-(2-cyclopenten-1-yl)-ethyl]magnesium as a single reaction product in high yield has been applied by Wilke and Rink[16] in the catalytic asymmetric synthesis of chaulmoograic acid (Scheme 1).

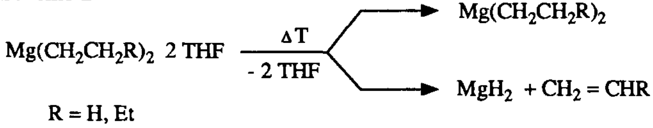
Scheme 1



Based on the results presented, it is concluded that the success of the synthesis of dialkylmagnesium compounds from magnesium, hydrogen, and 1-alkenes is not only dependent on the kind of the 1-alkene and on the hydromagnesation catalyst used, but also, to a decisive extent, on the quality of the magnesium hydride used, i.e. dependent on the way it is prepared as well as on its subsequent treatment. The high reactivity of magnesium hydride species prepared by homogeneous catalysis[5,6c,9,15] for the hydromagnesation of 1-alkenes and other applications[12,17,18] results from their high specific surface areas (70–180 m²/g), an oxide-free surface layer, which is a result of their preparation in an inert gas atmosphere[18], and a special ("fractal-like") morphology of MgH_2^* particles[19]. By appropriate choice of the hydrogenation catalyst and the hydrogenation reaction conditions the reactivity of MgH_2^* suspensions in THF can thus be varied and adjusted to that required for a specific reaction. A further method of modifying the reactivity of magnesium hydride reagents is given by the use of the dissolved catalytic magnesium hydride[9,10,16]. For the hydromagnesation of 1-alkenes the reactivity of the MgH_2^* suspension increases with decreasing hydrogenation temperature; the MgA–$CrCl_3$ catalyst appears to afford a more reactive MgH_2^* suspension than the MgA–$TiCl_4$ catalyst. Lower 1-alkenes are more prone to undergo hydromagnesation by MgH_2^* suspension than the higher ones.

Procedures for the isolation of Et_2Mg, Bu_2Mg, and Oct_2Mg as prepared from magnesium, hydrogen, and 1-alkenes from their THF solution in the catalyst- and as far as possible THF-free solid state are described in the experimental section (Experiments 1.2, 3.1 and Oct_2Mg, standard experiment). Thermolysis experiments in vacuo performed on Et_2Mg and Bu_2Mg (Experiments 1.3 and 3.2) have revealed that in the presence of transition metal catalysts it is not possible to completely remove the complexed THF without simultaneous partial elimination of 1-alkenes from dialkylmagnesium compounds (Scheme 2).

Scheme 2



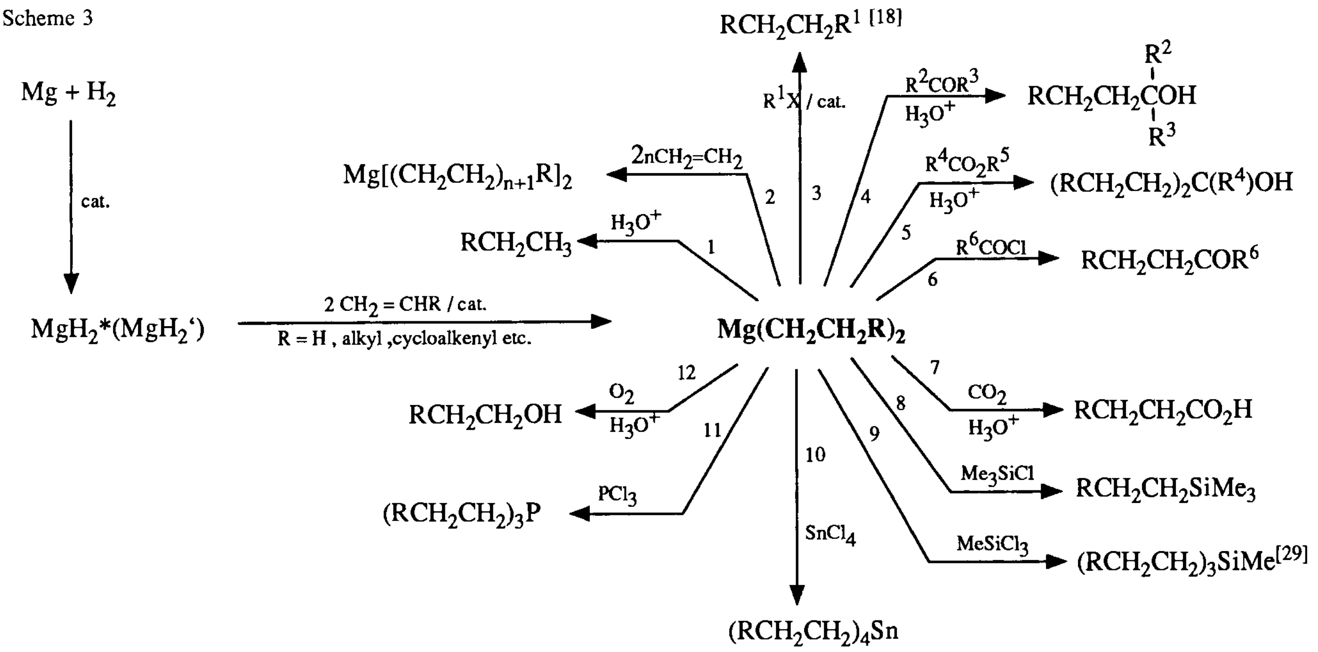
Application of Diorganomagnesium Compounds Prepared from Magnesium, Hydrogen, and 1-Alkenes in Organic and Organometallic Syntheses

A survey of the reactions carried out with diorganomagnesium compounds for the preparation of organic and organometallic compounds is given in Scheme 3. For these experiments, if not noted otherwise, Et_2Mg, Bu_2Mg, and Oct_2Mg (Experiments 1.3, 3.1 and standard Experiment, respectively) have been applied as prepared in situ.

A hydrolysis reaction affording *n*-alkanes (reaction no. 1) has been employed to characterize dialkylmagnesium compounds as prepared from magnesium, hydrogen, or 1-alkenes, or resulting from the growth reaction of Oct_2Mg with ethene (see below).

In the literature only a few reports inform about the growth reaction of magnesium alkyls with ethene[20]. In the present study, the growth reaction of THF-free, isolated Oct_2Mg with ethene in *n*-heptane under the influence of various electron donors (ethers, amines, and phosphanes) is investigated (reaction no. 2). The best results have been

Scheme 3



achieved with quinuclidine and diazabicyclooctane (DABCO) as electron donors in a 1:1 molar ratio with respect to Oct_2Mg at 123°C and 150 bar of C_2H_4 pressure. The molar distribution of *n*-alkanes obtained upon hydrolysis of the reaction mixture has proved to be in favorable agreement with the calculated distribution using the Poisson distribution function[21] (Figure 4). Simultaneously with the growth reaction, small amounts of 1-alkenes are formed as the result of the β-hydride elimination.

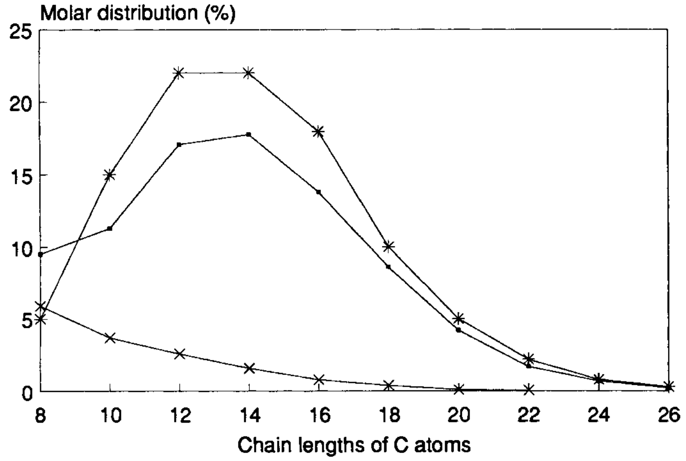


Figure 4. Composition of the growth reaction products of Oct_2Mg with ethene. —∗—, composition of *n*-alkyl chains calculated according to the Poisson distribution function[21] for the reaction of 3 mol of ethene with 1 equivalent of Oct_2Mg; —+—, molar distribution of *n*-alkanes produced as the result of the growth reaction of Oct_2Mg with ethene in the presence of quinuclidine and subsequent hydrolysis; —□—, composition of 1-alkenes formed in the same reaction

The Cu-catalyzed cross-coupling reaction of bis[2-(2-cyclopenten-1-yl)ethyl]magnesium with a tetrahydropyranyl-protected 11-bromoundecanol (reaction no. 3) has been applied as a C–C coupling step in the above mentioned synthesis of chaulmoograic acid[16].

Reactions of Grignard reagents with carbonyl compounds belong to the most widely used synthetic organic reactions. However, little is known about the corresponding reactions of dialkylmagnesium compounds[22]. Et_2Mg and Oct_2Mg react in situ with aliphatic or aromatic ketones (0.6:1 molar ratio) to afford tertiary alcohols in 63–84% yield (reaction no. 4; Table 7). Similarly, tertiary alcohols (reaction no. 5; Table 8) have been prepared in 86 and 68% yield by the reaction of ethyl propionate with Et_2Mg and Oct_2Mg (1:1.2 molar ratio), respectively. From these results it can be concluded that reactions proceed in the usual way, i.e. with alkylation of carbonyl compounds, in which both of the dialkylmagnesium alkyl groups are reactive. Reduction of carbonyl compounds, which is the preferred reaction with Grignard compounds in the presence of Cp_2TiCl_2[23], has not been observed.

The preparation of ketones in high yields by the addition of Grignard reagents (in excess) to a THF solution of acyl chlorides at −78°C has been reported[24]. Also, in a few cases, the addition of acyl chlorides to solutions of Grignard reagents at −70°C a 1:1 molar ratio has been found to produce ketones in satisfactory yields[25]. The Fe-catalyzed cross coupling reaction between Grignard reagents and acyl chlorides has an advantage over the non-catalyzed kind because it can be carried out at room temperature and because no excess of the Grignard compound is required[26].

The cross-coupling reaction of acyl chlorides with Oct_2Mg prepared in situ (reaction no. 6) was conducted both in the absence and presence of $Fe(acac)_3$ (acac = acetylacetonate) as a catalyst (Table 9). In the absence of the Fe catalyst, ethyl octyl ketone is formed in 71% yield when propionyl chloride is added dropwise to the Oct_2Mg solution at −73°C (2:1 molar ratio; Experiment 9.2). In contrast, the addition of an Oct_2Mg solution to benzoyl chloride at

$-73\,^{\circ}C$ (identical molar ratio; Experiment 9.6) leads to a low yield of octyl phenyl ketone. In the presence of the Fe catalyst the reaction of Oct_2Mg with acyl chlorides (1:2 molar ratio) affords octyl ketones in 57–67% yield (Experiments 9.1, 9.4, 9.5, and 9.7).

As an example of a carboxylic acid synthesis (reaction no. 7), pelargonic acid has been prepared in 78% yield by in situ carboxylation of Oct_2Mg.

The utility of dialkylmagnesium compounds prepared by the direct route to the synthesis of organic derivatives of silicium, tin, and phosphorus (reactions no. 8–11) has been demonstrated by several examples. Trimethyl-*n*-octylsilane containing only 0.3% of trimethylisooctylsilane is obtained in 90% yield by the reaction of Oct_2Mg with chlorotrimethylsilane (1:2 molar ratio) in situ. According to the patent literature[27], methyltrialkylsilanes, applicable as hydraulic fluid, can be prepared in high yields by treatment of Oct_2Mg or didecylmagnesium (Dec_2Mg), or a mixture of both, with trichloromethylsilane in the presence of cyanide or thiocyanate salts as catalysts. Tetra-*n*-butyltin of 96% purity is obtained in 83% yield from the in situ prepared Bu_2Mg and tin tetrachloride (2.4:1 molar ratio), while the corresponding reaction of pure isolated Oct_2Mg (1.28 molar ratio) affords tetra-*n*-octyltin in 95% yield and 99% purity. Tri-*n*-octylphosphane has been synthesized in nearly the same yield (84–85%) and purity (96–97%) either by reaction of the in situ prepared or pure isolated Oct_2Mg with phosphorous(III) chloride (1.8–1.9:1 molar ratio).

Oxidation of Grignard compounds by means of molecular oxygen is an established method for the preparation of hydroperoxides or alcohols[4b,28]. Saturated primary alkylmagnesium halides can be converted with dry air or oxygen via peroxide intermediates to the corresponding primary alcohols in 60–90% yield[29]. The insertion reaction of molecular oxygen in the Mg–C bond of [hydrotris(pyrazolyl)borato]magnesium alkyls has been recently reported[30]. However, the oxygenation reaction of dialkylmagnesium compounds is hardly known[31]. Of particular interest is therefore the finding that not only the pure isolated but also in situ prepared Oct_2Mg (in the presence of Cr and Zr catalysts) can be converted to *n*-octanol with only 0.3% of isooctanol[32] with molecular oxygen in 80–90% yield (reaction no. 12). The hydromagnesation of 1-alkenes using MgH_2^*[5,6c,15] or MgH_2'[9] and subsequent oxygenation of the resulting diorganomagnesium compounds thus opens a novel possibility for the highly regioselective conversion of 1-alkenes to primary alcohols. Known synthetic methods hitherto applied for that purpose are hydroboration[33], hydroalumination[34], hydrozirconation[35], and hydromagnesation by means of Grignard compounds[4b] of 1-alkenes followed by oxidative cleavage of the resulting metal-carbon bond.

As demonstrated by examples shown in Scheme 3, diorganomagnesium compounds prepared in situ from magnesium, hydrogen, and 1-alkenes ("one-pot reaction") can be employed for the synthesis of organic and organometallic compounds just as Grignard compounds. This synthetic route allows 1-alkenes to be used for the preparation of primary organomagnesium compounds instead of the corresponding primary halides. It is a complementary method for the Grignard procedure which can be applied in cases when 1-alkenes are more easily available or less expensive than the corresponding primary halides; in this method, however, only one equivalent of magnesium is required for the formation of one equivalent of a Mg–C bond. The synthesis is complicated by the necessity to employ an autoclave for the magnesium hydrogenation and because the handled MgH_2^* suspensions are pyrophoric (the handling of MgH_2' solutions is safer[9]).

In comparison with the hydromagnesation of 1-alkenes with Grignard compounds having β-hydrogens[4], the hydromagnesation procedure presented here offers the advantage of higher yields of organomagnesium compounds (because of the lower rate of 1-alkene isomerization versus MgH_2-to-1-alkene addition, Experiments 5.2 and 6.1–3, Experimental). Furthermore, the transition metal catalysts employed for the preparation of diorganomagnesium compounds do apparently not interfere significantly with their subsequent reactions.

To sum up our investigations: the hydromagnesation of 1-alkenes with MgH_2^* or MgH_2' represents a highly regio- and chemoselective method for converting 1-alkenes into the corresponding primary diorganomagnesium compounds; internal, endocyclic, and 1,1-disubstituted C=C bonds are not subjected to hydromagnesation by MgH_2^* or MgH_2'. Tertiary amine and ether groups (except for allylic ethers[36]) can be present in the molecule.

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Experimental

^1H-NMR: Bruker WP-80-FT. – IR: Nicolet 7000. – MS: Varian MAT CH 5, CH 7, or Finnegan MAT 8230. – GC/MS: combination of an F 22 Perkin-Elmer gas chromatograph with a Varian CH 7 A spectrometer. – GC: glass capillary columns with various stationary phases, commercial instruments, H_2 as the carrier gas, FID detection. – Elemental analyses: Dornis & Kolbe, Mülheim/Ruhr. – Vacuum definition: vacuum = 0.1 mbar; high vacuum = 10^{-3} mbar.

Starting Materials: Mg powder, Ventron 50 mesh or Eckart Werke PK-31, 270 mesh; anthracene, 99%, Rütgerswerke was applied without purification; H_2, 99.9%, Messer Griesheim; the saturated solution of anhydrous $MgCl_2$ in THF ($\approx$ 0.5 M) was prepared by the reaction of Mg powder with 1,2-dichloroethane in THF as described for the preparation of $MgBr_2$[37]. THF was heated at reflux over magnesium anthracene · 3 THF (MgA)[38] and distilled.

All reactions and operations with air-sensitive materials were performed under argon in air- and water-free solvents. **Caution:** *During catalytic hydrogenation of Mg powder and reaction of* MgH_2^* *with alkenes, especially with ethene and propene, the temperature of the reaction mixture should never exceed 100°C; at temperatures* $\geqslant$ *160–170°C serious explosions can occur due to reaction* *of Mg powder and/or* MgH_2^* *with THF.* MgH_2^* *suspensions in THF are pyrophoric.* MgH_2^* *suspensions in THF and concentrated solutions of dialkylmagnesium compounds in THF should be stored in metal containers, as reported in ref.*[17]

Et_2Mg (Tables 1 and 1A). Experiment 1.1: A 250-ml cylindrial two-necked flask served as the reaction vessel and glass insert for a 0.5-l non-magnetic high-grade steel autoclave of the flat bottom type (Figure 5). The flask was equipped with a three-way tap, a stopper, and a magnetic stirring bar. The temperature of the reaction mixture was measured by means of a thermocouple. 5.50 g (226 mmol) of Mg powder (50 mesh) and 0.52 g (2.9 mmol) of anthracene were placed in the flask, the flask was evacuated, filled with argon, and 100 ml of THF was added. The suspension, after addition of 2–3 drops of EtBr, was stirred at room temp. for 2–3 h until the formation of the orange MgA[38] precipitate was complete. Upon cooling (water bath, 15°C) and stirring 0.45 g (2.8 mmol) of anhydrous $CrCl_3$ (exothermic reaction, color change to dark brown!) was subsequently added to the reaction mixture. The glass vessel was inserted into the 0.5-l autoclave which had previously been thoroughly freed from air and moisture. With intensive magnetic stirring at 20–25°C (inner temperature!) the mixture was hydrogenated at an initial hydrogen pressure of 80 bar. After 20–22 h the hydrogen pressure dropped to 68 bar and then remained constant. The autoclave was depressurized and then pressurized (without stirring!) with 60 bar of ethene and subsequently heated with stirring to 85°C (inner temperature!) for 24 h. The autoclave was cooled down, slowly depressurized, opened and the content of the glass insert siphoned off through a metal U-tube into a graduated 250-ml Schlenk tube equipped with a three-way tap. (**Caution:** *Concentrated diethylmagnesium solutions in THF are pyrophoric on contact with water and air!*) Thus, 98 ml of a dark colored, slightly viscous Et_2Mg solution was obtained. 1.0 ml of the centrifuged Et_2Mg solution was cautiously dropped into an excess of 0.1 N HCl and the excess acid titrated back with 0.1 N KOH by using methyl red as indicator. This indicated that the Et_2Mg solution was 1.91 M, corresponding to 83% conversion of MgH_2^* to Et_2Mg.

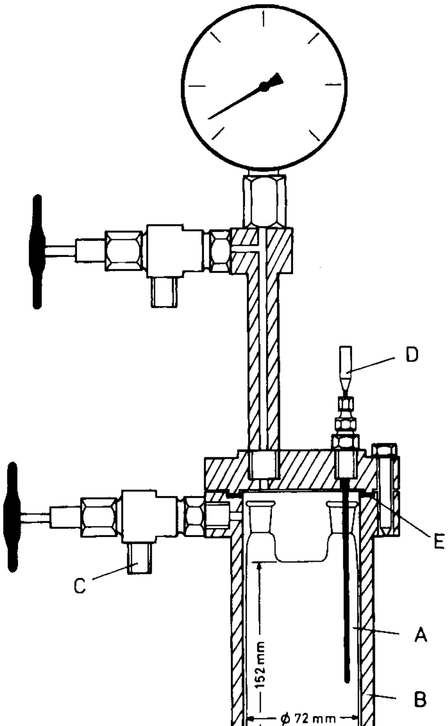

Figure 5. Glass vessel and autoclave used for the catalytic hydrogenation of magnesium and for hydromagnesation of lower 1-alkenes. A: glass vessel, B: autoclave, C: argon valve, D: thermocouple, E: teflon gasket

Three further experiments were carried out and analyzed in the same fashion as Experiment 1.1, except that the reaction times allowed for the reaction of MgH_2^* with ethene to proceed were 2.5, 6, and 70 h; the conversions of MgH_2^* to Et_2Mg were found to be 44, 71, and 82%, respectively. In order to explore the influence of the Cr catalyst on the reaction of MgH_2^* with ethene, in a further experiment, conducted and analyzed as Experiment 1.1, after the hydrogenation step the MgH_2^* was separated from the reaction solution (containing the Cr catalyst) by filtration and washing with THF and thereafter suspended in 100 ml of fresh THF. The reaction with ethene at 85°C and 60 bar (initial) ethene pressure resulted in a 20% conversion of MgH_2^* to Et_2Mg after 48 h.

Experiment 1.2: The starting materials were 20.0 g (0.82 mol) of Mg powder (50 mesh), 100 ml of THF, 0.18 g (1.0 mmol) of anthracene, and 0.16 g (1.0 mmol) of $CrCl_3$. The hydrogenation of Mg powder (80 bar H_2 pressure/20–25°C/21 h) was carried out as described in Experiment 1.1 except that a 1-l size high-grade steel autoclave of the flat bottom type *without* a glass insert was used. After the hydrogenation step, the autoclave was depressurized, flushed with argon and opened. To the MgH_2^* suspension in the autoclave 250 ml of THF was added, and subsequently the mixture was stirred with 1.90 g (8.1 mmol) of $ZrCl_4$. The autoclave was charged with ethene (60 bar) without stirring and then heated with stirring to 85°C for a period of $1\frac{1}{2}$ h. (**Caution:** *The reaction of* MgH_2^* *with ethene in the presence of the Zr catalyst is very vigorous and exothermic; heating of the reaction mixture above 100°C, especially when working on a larger scale, must be strictly avoided!*) The autoclave was cooled, slowly depressurized, opened and the content of the autoclave transferred through a metal U-tube to a graduated 0.5-l Schlenk tube equipped with a three-way tap. (**Caution:** See Experiment 1.1!) The reaction product consisted of 410 ml of a dark brown slightly turbid solution of Et_2Mg in THF. According to the acidimetric determination of Mg^{2+} in a sample of a centrifuged and hydrolyzed solution (see Experiment 1.1), the solution contained 97% of the Mg used in the experiment. 5.0 ml of the centrifuged solution, after evaporation of the solvent and drying of the residue at 120°C in vacuum, yielded on alcoholysis (cyclohexanol) 450 ml of gas (20°C, 1 bar) composed of 96% of C_2H_6 and 4% of C_4H_{10}, according to mass spectrometry. From these data a molarity of the solution of 1.88 mol/l and a yield of dialkylmagnesium of 94% (based on the Mg used) could be calculated.

Isolation of Catalyst- and THF-Free Et_2Mg: 300 ml of the Et_2Mg solution prepared as described above was evaporated to dryness in vacuo and the residue heated to 120°C for 1 h in high vacuum. Then 0.68 g of the black viscous residue yielded on protolysis with ca. 3 ml of cyclohexanol and subsequent distillation in vacuo 1.13 g of a liquid containing 7.3 wt-% THF, according to GC analysis. $Et_2Mg:THF \approx 1:0.12$. The viscous residue was dissolved in 1.3 l of pentane and upon the addition of 13 ml of THF ($Et_2Mg:THF \approx 1:0.4$) heated to reflux while stirring for 10 min. The solution was filtered (glass frit) from the black precipitate (catalyst and small amounts of MgH_2^*), and the filtrate was kept overnight at −10°C, whereby 5–10 ml of a viscous brown oil separated from the solution, while the supernatant pentane solution was only slightly yellow colored. The pentane phase was siphoned off, evaporated to

Table 1. Et_2Mg from magnesium, hydrogen, and ethene

Expt.	Hydrogenation of Mg[a]			Reaction of MgH_2^* with ethene[b]				
No.	Mg powder g (mol)	$MgCl_2$ [mol-%]	Cat. [mol-%]	THF[c] [ml]	$ZrCl_4$ [mol-%]	C_2H_4 [bar]	Time [h]	Yield of Et_2Mg [%]
1.1[d]	5.50 (0.23)	–	$CrCl_3$ (1.2)	–	–	60	24	83[e]
1.2[d]	20.0 (0.82)	–	$CrCl_3$ (1)	250	1	60	1.5	97[e] (94)[f]
1.3[g]	15.0 (0.62)	7	$TiCl_4$ (1)	–	–	30	4	97[f]
1.4	Reaction	of isolated	MgH_2^* with C_2H_4 in Et_2O (see text)					88[e]

[a] Hydrogenations were performed in 100 ml of THF in the presence of 1 mol-% of anthracene. — [b] At 85°C (Experiments 1.1 and 1.2) or 75°C (Experiment 1.3). — [c] Addition of THF after the hydrogenation is completed. — [d] Conditions for hydrogenation: 20–25°C/80 bar H_2, 20–21 h. — [e] Based on acidimetric titration. — [f] Based on the amount of C_2H_6 evolved on protolysis. — [g] Hydrogenation conditions: 60 bar of H_2 pressure, 57–60°C, 2.5 h.

Table 1A. The time dependence of the THF content decreases (in mol-%; $Et_2Mg \cdot 1$ THF = 100 mol-%) and that of the MgH_2 content increases (numbers in brackets; in mol-%) of $Et_2Mg \cdot 2$ THF samples heated to 130, 150, and 160°C in high vacuum

Time[h^{min}]	0	0^{50}	1^{00}	1^{50}	2^{00}	3^{00}	3^{25}	4^{00}	6^{40}
130 °C			12(5)		7	6(11)		0.8(17)	
150 °C	21	10(6)		4(13)			1(15)		0.4
160 °C			7(18)		0.7(20)				

dryness in vacuo and the solid residue heated to 120°C for 1 h in high vaccum affording 39.6 g of Et_2Mg as a pale yellow pyrophoric powder (80% yield based on Mg).

$C_4H_{10}Mg$ (82.4)
Calcd. C 58.28 H 12.20 Cr 0.00 Mg 29.50 Zr 0.00
Found C 58.26 H 12.15 Cr 0.006 Mg 29.66 Zr 0.004

The determination of residual THF in Et_2Mg thus obtained was carried out as described above: Et_2Mg:THF = 1:0.01.

Experiment 1.3 (Hydrogenation of Mg in the Presence of $MgCl_2$ as a Cocatalyst): 15.0 g (0.62 mol) of Mg powder (50 mesh) and 1.09 g (6 mmol) of anthracene were placed in a two-necked 250-ml flask equipped with a three-way tap and a magnetic stirring bar. The flask was evacuated, filled with argon and charged with 100 ml of a 0.42 M $MgCl_2$ solution in air-free, dry THF (see Starting Materials) and with a few drops of EtBr. After stirring for 10–15 min at room temp., the color of the solution turned deep blue due to the formation of the Mg_2Cl_3-anthracene radical anion complex[39]. Then 2.11 g (6.0 mmol) of the complex $TiCl_4 \cdot 2$ THF was added to the suspension (weakly exothermic reaction) which was stirred for a further 10 min. The content of the flask was now siphoned off through a metal U-tube into the 0.5-l non-magnetic steel autoclave illustrated in Figure 5 which has previously been thoroughly freed from air and moisture. With magnetic stirring the autoclave was then pressurized with 60 bar of hydrogen. The hydrogenation was carried out with magnetic stirring at 60°C until the hydrogen pressure remained constant at about 30 bar (ca. 2.5 h). The autoclave was brought to atmospheric pressure, then pressurized (without stirring!) with 30 bar of ethene and subsequently heated while stirring at 75°C (inner temp.) for altogether 4 h. After 1 h, when the ethene pressure had dropped to 2–3 bar, the autoclave was again pressurized with ethene (30 bar) and 2.5 h later, after the second pressurizing with ethene, the pressure remained constant. The autoclave was cooled down, slowly depressurized and the content of the autoclave siphoned off through a U-tube into a graduated 250-ml Schlenk tube equipped with a three-way tap (**caution**, see Experiment 1.1!). Thus, 180 ml of the dark colored, slightly viscous clear[40] solution of Et_2Mg was obtained. According to the acidimetric titration of magnesium after hydrolysis of 1.0 ml of the solution (see Experiment 1.1), the solution was 3.4 M. After removal of the THF from 1.0 ml of the solution in vacuo, the residue yielded on protolysis with 2-propanol 159 ml of gas (20°C, 1 bar) composed of 99% of ethane and 1% of butane (MS analysis), corresponding to a 97% yield of Et_2Mg (based on Mg).

Investigation of THF Dissociation and Simultaneous Ethene Elimination from $Et_2Mg \cdot 2$ THF at 130, 150, and 160°C in vacuo (Scheme 2 and Table 1A): Three portions of the above described Et_2Mg solution (70 ml each) were evaporated to dryness in vacuo, and the solid residue was slowly heated and then kept in high vacuum at 130, 150, and 160°C, respectively, for several hours. At definite intervals samples (ca. 1 g) were taken from the solid, protolyzed by the addition of cyclohexanol, and the evolved gas (C_2H_6 + H_2) was analyzed by mass spectrometry for its H_2 content; the volatile components of the protolyzed samples were then distilled off in vacuo and the distillates analyzed for their THF content by gas chromatography.

Experiment 1.4: 6.95 g of MgH_2^*, prepared by catalytic hydrogenation of Mg powder as described in Experiment 1.1, was separated from the reaction solution by filtration and washing with THF, then dried in high vacuum at 80°C for 3 h. The MgH_2^* thus obtained was suspended in 100 ml of Et_2O and after the addition of 4.3 mmol of $ZrCl_4$ allowed to react with ethene (40 bar) at 70°C for 10 h. According to acidimetric titration of magnesium in a sample of the Et_2Mg solution after hydrolysis (Experiment 1.1), the conversion of MgH_2^* to Et_2Mg was 88%. (Small amounts of polyethylene were also formed during the experiment.)

Table 2. Pr_2Mg from magnesium, hydrogen, and propene

Expt.	Hydrogenation of Mg[a]			Reaction of MgH_2^* with propene[b]				
No.	Mg powder g (mol)	Anthr. [mol-%]	Cat. (mol-%)	THF[c] [ml]	Cat. (mol-%)	C_3H_6 g (mol)	Time [h]	Yield of[d] Pr_2Mg [%]
2.1	5.50 (0.23)	2	$TiCl_4$ (2)	–	–	30 (0.71)	72	95
2.2	5.50 (0.23)	5	$TiCl_4$ (5)	–	–	32 (0.72)	70	98
2.3	5.50 (0.23)	1.3	$CrCl_3$ (1.3)	100[e]	Cp_2TiCl_2 (5)	30 (0.71)	70	93
2.4	20.0 (0.81)	1	$CrCl_3$ (1.3)	250	$ZrCl_4$ (1)	119 (21)	2¼	83

[a] Hydrogenations were performed in 100 ml of THF; conditions for hydrogenation: 20–25°C/90 bar H_2, 21–26 h. – [b] At 85°C. – [c] Addition of THF after the hydrogenation is complete. – [d] Based on acidimetric titration. – [e] See text pertaining to Experiment 2.3.

Table 3. Bu_2Mg from magnesium, hydrogen, and 1-butene

Expt.	Hydrogenation of Mg			Reaction of MgH_2^* with 1-butene[a]				
No.	Mg powder g (mol)	$MgCl_2$ [mol-%]	Cat. (mol-%)	THF[b] [ml]	$ZrCl_4$ [mol-%]	1-Butene [g]	Time [h]	Yield of Bu_2Mg [%]
3.1[c]	20.0 (0.81)	–	$CrCl_3$ (1)	250	1	180	4	79[d]
3.2[e]	10.0 (0.41)	8.3	$TiCl_4$ (1.2)	–	–	70	3	86[f]

[a] At 85–98°C. – [b] Addition of THF after the hydrogenation is complete. – [c] THF: 100 ml; anthracene: 1 mol-%; hydrogenation: 60 bar H_2, 25°C, 21 h. – [d] Based on n-C_4H_{10} evolved on hydrolysis. – [e] THF: 80 ml; anthracene: 1 mol-%; hydrogenation: 60 bar H_2, 60°C, 2½ h. – [f] Based on acidimetric titration of Mg^{2+}.

Pr_2Mg: Starting materials, reaction conditions and reaction products are listed in Table 2.

The Experiments 2.1 and 2.2 were caried out and the reaction mixtures analyzed as described for Expt. 1.1, except that after hydrogenation of Mg and release of the H_2 pressure the autoclave was pressurized with cooling (0°C) and stirring with propene contained in a pressure cylinder. The amount of propene (in g) dissolved in the reaction mixture during this procedure was determined by weighing the autoclave.

Experiment 2.3 was carried out and the reaction mixture analyzed as described for Experiment 1.1, except that, after hydrogenation of Mg, MgH_2^* was separated from the reaction solution by filtration and washing with THF and then suspended in 100 ml of fresh THF; 2.79 g (11.2 mmol) of Cp_2TiCl_2 as a catalyst and propene (see Experiments 2.1 and 2.2) were then added to the reaction mixture.

In Experiment 2.4, hydrogenation of Mg was carried out as described for Experiment 1.2; propene was added to the reaction mixture as described for Experiment 2.1 and 2.2. 430 ml of a turbid 1.57 M Pr_2Mg solution in THF was obtained as reaction product.

Bu_2Mg: Starting materials and reaction conditions are compiled in Table 3.

Experiment 3.1 was carried out and the reaction mixture analyzed as described for Experiment 1.2, except that after the hydrogenation of Mg and release of the H_2 pressure the autoclave was pressurized with cooling (–10°C) and with stirring with 1-butene which was dried with Et_2AlOEt in a pressure cylinder. The amount of 1-butene (in g) dissolved in the reaction mixture was determined by weighing the autoclave. 566 ml of a dark brown, slightly turbid solution of Bu_2Mg in THF was obtained. According to acidimetric titration of Mg^{2+} after hydrolysis of 1.0 ml of the centrifuged solution, the solution contained 90% of Mg used for the experiment. Based on the amount of n-butane evolved on alcoholysis of 5.0 ml of the solution evaporated to dryness (cf. Experiment 1.2), the solution was 1.14 M with respect to Bu_2Mg (79% yield related to Mg).

Isolation of Catalyst- and THF-Free Bu_2Mg: 350 ml of the solution was evaporated to dryness in vacuo and the residue heated to 115°C in high vacuum for 70 min. 0.70 g of the black viscous residue after protolysis with n-butanol (ca. 4 ml) and subsequent distillation of the volatile components in vacuo yielded 1.49 g of a liquid containing 3.8 wt-% of THF (GC analysis): Bu_2Mg:THF = 1:0.17. Then 1.2 l of pentane was added to the crude Bu_2Mg and the mixture heated to reflux for 15 min with stirring. The warm suspension was filtered off from the black precipitate (catalyst, MgH_2^*, Bu_2Mg); the precipitate was suspended in 1.0 l of pentane and 3 ml of THF, and the suspension heated for 15 min under reflux and then filtered again. The two filtrates were each concentrated to a volume of 200 ml, combined, and the solution was kept overnight at –10°C, whereby Bu_2Mg separated from the solution as a pale beige precipitate. The precipitate was filtered off from the solution at –10°C, washed twice with 20 ml of cold pentane, dried in vacuo, and then heated to 115°C in high vacuum for 1 h. 51.2 g of Bu_2Mg (73% related to Mg) was obtained as a pale yellow solid. Determination of residual THF in Bu_2Mg thus prepared (carried out as described above): Bu_2Mg:THF = 1:0.013.

$C_8H_{18}Mg$ (138.5)					
Calcd.	C 69.36	H 13.10	Cr 0.00	Mg 17.54	Zr 0.00
Found	C 68.90	H 13.06	Cr 0.003	Mg 17.98	Zr 0.005

In Experiment 3.2 the hydrogenation of Mg in the presence of $MgCl_2$ was performed in the same manner as described for Experiment 1.3; after the hydrogenation step and release of H_2 pressure, the autoclave was pressurized with 1-butene as described in Experiment 3.1. 147 ml of a dark colored turbid solution of Bu_2Mg was obtained. Based on acidimetric titration of Mg^{2+} in the aqueous solution obtained by centrifugation of the Bu_2Mg solution as well as by hydrolysis of 1.0 ml of the centrifuged solution, the solution was 2.37 M (85% yield of Bu_2Mg related to Mg). Protolysis of the Bu_2Mg solution (after evaporation of THF) afforded only *n*-butane as a gaseous product.

The time dependence of the thermal THF dissociation from $Bu_2Mg \cdot 2$ THF (Scheme 2 and Table 3A) in Experiment 3.2 was determined as described for Et_2Mg (Experiment 1.3).

Table 3A. The time dependence of the THF decreases (in mol-%; $Bu_2Mg \cdot 1$ THF = 100 mol-%) and that of the MgH_2 content increases (numbers in brackets; in mol-%) of $Bu_2Mg \cdot 2$ THF samples heated to 120, 138, and 150°C in high vacuum

Time [h^{min}]	0	1^{00}	1^{15}	2^{00}	2^{45}	4^{20}	7^{20}
120 °C	37(0)		21(4)		8.2	4.9(11)	
138 °C			11(7)		3	1(14)	0.7(26)
150 °C		12.6(14)		3.5(25)			

EtBuMg: Starting materials and reaction conditions are listed in Table 4.

Experiment 4.1: The hydrogenation of Mg and the reaction of MgH_2^* with ethene and 1-butene were carried out as described in Experiments 1.2 and 3.1 by employing a 0.5-l high-grade steel autoclave having a flat bottom (Figure 5). The dark brown solution of EtBuMg (248 ml) was evaporated to dryness in vacuo and the residue heated to 120°C in high vacuum for 10 h. The black solid residue was suspended in 700 ml of hexane and the suspension heated with stirring to 60°C for 15 min. The warm suspension was filtered and the filter cake washed with hexane to afford 750 ml of a pale yellow, viscous solution of EtBuMg. 3.0 ml of the solution evolved on hydrolysis 68 ml of gas (20°C, 1 bar) of the following composition (MS analysis): C_2H_6 59.8, C_4H_{10} 34.4, C_4H_8 2.7, H_2 3.1%. Based on these data the composition of the diorganomagnesium compound in the solution was $(Et)_{1.2}(Bu)_{0.8}Mg$, yield 71% (related to Mg).

Experiment 4.2 (Hydrogenation of Mg in the Presence of $MgCl_2$ as a Cocatalyst): The hydrogenation of Mg and the reaction of MgH_2^* with ethene and 1-butene were carried out as described in Experiments 1.3 and 3.1 (**caution**, see Experiment 1.3!). The dark brown, slightly turbid solution obtained was filtered to afford 163 ml of EtBuMg solution. Based on the acidimetric titration of Mg^{2+} in 1.0 ml of this solution after hydrolysis, the solution was 2.34 M (94% yield, based on Mg).

For the removal of the complexed THF from EtBuMg, the solution was evaporated to dryness in vacuo, the oily residue slowly heated and dried in vacuo at 120–130°C for 10 h. The black solid residue was suspended in hexane (1 l of hexane per 100 g of residue) and, after the addition of 2 mol-% of Et_3Al (related to Mg), the suspension was refluxed shortly and filtrated. In this manner, a pale yellow and almost THF-free solution of EtBuMg in hexane was obtained.

Oct_2Mg (Figures 1 and 2, Table 5): In experiments pertaining to Figure 1, hydrogenation of Mg powder (50 mesh; 10.0 g, 0.41 mol) was conducted in 50 ml of THF with the aid of the MgA—$CrCl_3$ catalyst as described in Experiment 1.1. The hydrogenation at 20–25°C/80–90 bar H_2 (initial) pressure required 17–18 h for completion. After the hydrogenation steps, the autoclave was depressurized, flushed with argon, opened, and the MgH_2^* suspension transferred (**caution:** MgH_2^* suspensions are pyrophoric!) to a 0.5-l three-necked flask provided with a three-way tap, a magnetic stirring bar and a reflux condenser; the latter was equipped with a copper cooling coil and surmounted by an argon bubbler. For each experiment, to the thus prepared suspension of MgH_2^* in THF were added 130 ml of THF, 1 mol-% (related to Mg) of the specific hydromagnesation catalyst (see Figure 1) as well as 150 ml (107.0 g, 0.96 mol) of 1-octene (97% purity; 3% *n*-octane), and the stirred mixture was heated to reflux. After a definite period of time 3.0-ml samples were taken from the solution[41], centrifuged, and the conversion of MgH_2^* to Oct_2Mg after hydrolysis of the samples was determined acidimetrically, as described for Experiment 1.1. During the reaction an increase in the boiling point of the mixture was observed. The course of conversion of MgH_2^* to Oct_2Mg as a function of time for various hydromagnesation catalyts is graphically represented in Figure 1.

Experiments pertaining to Figure 2 were carried out as described above, except that the hydrogenation of Mg powder was performed by using various catalysts as well as different temperatures (see Figure 2) while, for each experiment, $ZrCl_4$ (1 mol-%) was added after hydrogenation as a hydromagnesation catalyst. For the experiment designated by –□– in Figure 2, MgH_2^* was separated from the catalyst solution by filtration, washed with THF, dried in vacuum and then suspended in 180 ml of fresh THF; after the addition of 1 mol-% of $ZrCl_4$ and 150 ml of 1-octene, the mixture was heated to reflux and analyzed as in other experiments pertaining to Figures 1 and 2.

In the experiments listed in Table 5 and Figure 2 (–×– and –◇–), the reaction of MgH_2^* with 1-octene was conducted as described above, except that the hydrogenation of Mg powder was

Table 4. EtBuMg from magnesium, hydrogen, ethene, and 1-butene

Expt.	Hydrogenation of Mg			Reaction of MgH_2^* with C_2H_4/C_4H_8				
No.	Mg powder g (mol)	$MgCl_2$ [mol–%]	Cat. (mol–%)	THF[a] [ml]	$ZrCl_4$ [mol–%]	C_2H_4/C_4H_8 [g]	Time [h]	Yield of EtBuMg [%]
4.1[b,c]	12.3 (0.5)	–	$CrCl_3$ (1)	160	1	15/31	12	71[d]
4.2[b,e]	10.0 (0.4)	8	$TiCl_4$ (1)	–	1.2	11/48	1½	94[f]

[a] Amount of THF added after the hydrogenation is complete. — [b] THF: 60 ml; anthracene: 1 mol-%. — [c] Hydrogenation: 80 bar H_2, 25°C, 26 h; reaction of MgH_2^* with a C_2H_4/C_4H_8 mixture at 75°C. — [d] Based on the amount of C_2H_6/C_4H_{10} evolved on hydrolysis. — [e] Hydrogenation: 60°C/60 bar H_2, 3 h; reaction of MgH_2^* with C_2H_4/C_4H_8 mixture at 94°C. — [f] Based on acidimetric titration of Mg^{2+}.

Table 5. Oct_2Mg from magnesium, hydrogen, and 1-octene (hydrogenation of Mg in the presence of $MgCl_2$ as cocatalyst)

Expt.	Hydrog. of Mg[a]		Reaction of MgH_2^* with 1-octene[b]							
No.	Cat.	$MgCl_2$ [mol-%]	THF[c] [ml]	$ZrCl_4$ [mol-%]	convers. of MgH_2^* [%] / reaction time [h]					Figure 2
5.1	MgA–$TiCl_4$	9	100	1	18	31	58	76	84	—x—
					½	1	2	4	10	
5.2	MgA–$CrCl_3$	5	140	1	10	31	76	80	91	—◊—
					1	2	5	7	23	
5.3	MgA–$TiCl_4$	9	100	2.5	89					
					5					
5.4	MgA–$TiCl_4$	9	100	1	80	83	83	88		
					3	5	7	21		

[a] For each experiment 10.0 g (0.4 mol) of Mg powder in 50–75 ml of THF and 1 mol-% of the respective catalyst were used; hydrogenations of Mg powder were complete within 2–2.5 h at 60°C/60 bar H_2 (Experiments 5.1, 5.3, and 5.4) or 25°C (Experiment 5.2). — [b] For each experiment 150 ml (107.0 g, 0.96 mol) of 1-octene was used; the boiling temperature of the THF/1-octene mixture served as a reaction temperature (Experiment 5.1–5.3); for expt. 5.4 the reaction took place at 95–100°C in an autoclave. — [c] Amount of THF added after the hydrogenation step.

performed in the presence of $MgCl_2$ as a cocatalyst (cf. Experiment 1.3); hydrogenation was thus completed within 2–2.5 h. For experiment 5.2, 5.0 ml of the resulting Oct_2Mg solution (reflux period 23 h; conversion of MgH_2^* 91%; total volume of the solution 340 ml) was evaporated to dryness in vacuo and the distillate analyzed by gas chromatography. Composition of the C_8 fraction (0.43 g): 1-octene 68.7, *trans*-2-octene 11.8, *cis*-2-octene 11.5, *n*-octane 7.3, *trans*-3-octene 0.2, *cis*-3-octene 0.5%. Another 30.0 ml of the Oct_2Mg solution was evaporated to dryness in vacuo, 5 ml of toluene added to the residue and the Oct_2Mg hydrolyzed by the addition of 2-propanol and water. The aqueous solution was neutralized with 5 N HCl, separated from the toluene solution and extracted several times with toluene. The combined extracts were distilled in vacuo and the distillate, after the addition of *n*-decane as an internal standard, analyzed for *n*-octane by gas chromatography. In the C_8 fraction, 7.22 g of *n*-octane and 0.09 g of 1-octene were determined. The yield of 87% of Oct_2Mg (related to Mg) was calculated based on the *n*-octane amount.

Isolation of Catalyst- and THF-Free Oct_2Mg: The standardized experiment (Figures 1 and 2, –⧖–) was repeated with three times greater amounts of starting material and catalyst (30.0 g of Mg powder etc.). The conversion of MgH_2^* to Oct_2Mg after refluxing for 19 h was determined to be 86% according to acidimetric titration. 950 ml of the total 1.0-l Oct_2Mg solution was evaporated to dryness in vacuo and the black, viscous oily residue dried in high vacuum for 30 min at room temp., then at 80°C for 1 h. After heating in high vacuum, the THF content of the solid residue was determined (see Experiment 1.2) and found to be Oct_2Mg:THF ≈ 1:0.1. The residue was suspended in 650 ml of pentane, the suspension heated for 20 min under reflux and the pentane solution of Oct_2Mg separated from the catalyst and MgH_2^* by filtration. The filtrate was kept at –10 to 0°C for 1 h in which Oct_2Mg separated from the solution as a voluminous precipitate. After filtration at 0°C, washing with cold pentane and drying in vacuo, Oct_2Mg (201.0 g, 69% to Mg) was obtained as an almost colorless powder. THF content (see Experiment 1.2): Oct_2Mg:THF = 1.0:0.02.

$C_{16}H_{34}Mg$ (250.8)
Calcd. C 76.64 H 13.67 Cr 0.00 Mg 9.69 Zr 0.00
Found C 76.44 H 12.94 Cr 0.03 Mg 9.67 Zr 0.01

In order to remove traces of heavy metals, 104.0 g of Oct_2Mg thus prepared was dissolved in a boiling mixture of 200 ml of pentane and 2 ml of THF and the Oct_2Mg isolated from the solution by crystallization as described above. THF content (see Experiment 1.2): Oct_2Mg:THF = 1.0:0.01. Yield: 93.0 g of colorless Oct_2Mg of the following composition: C 75.96, H 13.05, Mg 10.21, Cr, Zr <0.001%.

Dec_2Mg: The preparation of Dec_2Mg (Table 6 and Figure 3) was carried out with solubilized magnesium hydride (MgH_2'); in Experiments 6.1 and 6.2 Oct_2Mg and in Experiment 6.3 quinuclidine was applied as solubilizing agent[9,10]. For Experiment 6.1, an excess of 15% of 1-decene over MgH_2' and for Experiments 6.2 and 6.3 an excess of 15% of MgH_2' over 1-decene was used. General procedure: The MgH_2' solution was placed in a three-necked flask equipped with a reflux condenser (copper cooling coil!) and a dropping funnel. After the addition of 0.23 g (1.0 mmol) of $ZrCl_4$, the solution was heated to reflux and 1-decene (Table 6; purity 99.4%) added dropwise and with stirring within 2½ h[42]. After completion of the 1-decene addition, at fixed intervals, 1.0-ml samples were taken from the boiling solution[41], protolyzed by the addition of EtOH and the evolved H_2 amount was measured. The decrease in the amount of H_2 evolved on protolysis of successive samples was taken as a rough measure of the progress of the reaction. The protolyzed samples were centrifuged, and the clear solution was analyzed for decane, 1-decene, *cis*- and *trans*-2-decene by gas chromatography[10]. The % conversion of MgH_2' to Dec_2Mg represented in Figure 3 was calculated on the basis of the decane content of the samples. The sum of the amounts of decane, 1-decene as well as *cis*- and *trans*-2-decene gave a satisfactory mass balance, indicating that these were the only products formed. After reaction times of 23–27 h, the non-reacted C_{10} hydrocarbons were still found to be composed to 58–74% of 1-decene, the rest was *cis*- and *trans*-decene[10].

$Pentadec_2Mg$: The hydrogenation of 5.62 g (0.23 mol) of Mg powder (50 mesh) in 50 ml of THF using 1 mol-% of the MgA–$CrCl_3$ catalyst at 20–25°C/50 bar H_2 was performed as described for Experiment 1.1. After the addition of 50 ml of THF, 0.65 g (2.8 mmol) of $ZrCl_4$ and 114 ml (0.42 mol) of 1-pentadecene to the MgH_2^* suspension, the mixture was heated under reflux for 4 h 10 min, as described for the preparation of Oct_2Mg (during this time an increase from 76 to 81 °C in the boiling point of the mixture was observed). Based on acidimetric titration (see Experiment 1.1), the conversion of MgH_2^* to $Pentadec_2Mg$ after 2⅓ h was 91% and after

Table 6. Dec_2Mg from solubilized magnesium hydride (MgH_2') and 1-decene

Expt. No.	MgH_2' [mmol]	THF [ml]	$ZrCl_4$ [mmol]	1–decene [mmol]	Fig. 3
1	100[a]	43.5	1.0	230	—△—[b]
2	115[a]	50	1.0	200	—+—[c]
3	115[d]	50	1.0	197	—□—[c]

[a] MgH_2' solubilized by Oct_2Mg. — [b] MgH_2' conversion was found to be 91.5% after a reaction time of 23 h. — [c] MgH_2' conversion was found to be 89–90% after a reaction time of 27 h. — [d] MgH_2' solubilized by quinuclidine.

4 h 10 min 95% (related to 1-pentadecene). 5.0 ml of the $Pentadec_2Mg$ solution was evaporated to dryness in vacuo and the residue protolyzed by the addition of EtOH. After vacuum distillation, the distillate was analyzed by gas chromatography. Based on the amount of *n*-pentadecane in the distillate, the conversion of MgH_2^* to $Pentadec_2Mg$ after 4 h and 10 min was 91%.

Growth Reaction of Oct_2Mg with Ethene: 4.58 g of isolated solid Oct_2Mg (see above; 90.1% content of Oct_2Mg based on the amount of *n*-octane formed on hydrolysis) was dissolved in 80 ml of *n*-heptane and then 1.83 g of quinuclidine (Oct_2Mg : quinuclidine = 1 : 1) was added to the solution. The mixture was transferred to a 0.5-l non-magnetic, high-grade steel autoclave (Figure 5) and pressurized with 80 bar ethene. The content of the autoclave was heated with stirring to 123°C for 12 h. After hydrolysis and neutralization of the reaction mixture (dil. HCl) the organic layer was separated from the aqueous one. The organic layer, upon the addition of n-C_{13} and n-C_{25} alkanes as internal standards, was analyzed by gas chromatography. The molar distribution of *n*-alkenes and 1-alkenes is shown in Figure 4. In accordance with the composition of the reaction products, an average of 2.6 mol of ethene had reacted with one equivalent of Oct_2Mg by insertion into the Mg–C bonds. The sum of 1-alkenes amounted to 15% of the total sum of *n*-alkanes and 1-alkenes.

Table 7. Tertiary (secondary) alcohols from Alk_2Mg compounds and ketones (benzaldehyde) in a ca. 0.6 : 1 molar ratio in THF at room temp. or 60°C (Experiment 7.5)

Exp. No.	Alk_2Mg comp. (mmol)	Carbonyl comp. (mmol)	React. time [h]	Reaction product (yield [%])
1	Et_2Mg (59)	PhCHO (98)	2	PhEtCHOH (84)
2	Et_2Mg (44)	EtCOEt (76)	3	Et_3COH (70)
3	Et_2Mg (46)	PhCOEt (75)	1	$PhEt_2COH$ (81)
4	Oct_2Mg (48)	EtCOEt (76)	12	$OctEt_2COH$ (63)
5	Oct_2Mg (46)	PhCOEt (75)	3	PhOctEtCOH (71)

Tertiary (Secondary) Alcohols from Alk_2Mg Compounds and Ketones (Benzaldehyde) (Table 7): The Et_2Mg (Experiment 1.3) and Oct_2Mg solutions (standardized experiment) were, if necessary, separated from small amounts of MgH_2^* by filtration and diluted with THF to a concentration of 1.2 M. Freshly distilled carbonyl compounds were added dropwise to stirred solutions of Alk_2Mg compounds, and the mixtures were cooled with an ice bath or to −78°C (Experiment 7.1). After an initial exothermic reaction, the reaction mixtures were stirred at room temp. or 60°C (Experiment 7.5) for the periods of time listed in Table 7. THF was distilled off in vacuo, 30 ml of toluene added and the reaction mixture hydrolyzed and neutralized with 5 N HCl. The organic layer was separated from the aqueous layer and the latter extracted several times with toluene. The combined extracts were dried with Na_2SO_4. For Experiments 7.1–7.3 the products (alcohols) were distilled in vacuo together with the solvent. The yield of the alcohol in toluene solutions, after the addition of *n*-alkanes as internal standards, was determined by gas chromatography. In Experiments 7.4 and 7.5, toluene was distilled off and the alcohols were distilled in high vacuum. 3-Ethyl-3-undecanol (Experiment 7.4; 9.52 g) was obtained with 98% purity (GC analysis) and identified by IR, ^1H-NMR and mass spectra. 3-Phenyl-3-undecanol (Experiment 7.5; 15.57 g) was obtained with 84% purity (GC analysis).

Tertiary Alcohols from Alk_2Mg compounds and Ethyl Propionate (Table 8): The Et_2Mg (Experiment 1.3) and the Oct_2Mg solution (standardized experiment), separated from MgH_2^* by filtration, were diluted with THF to concentrations of 2.2 (Experiment 8.1) and 1.2 M (Experiment 8.2), respectively. Ethyl propionate was added dropwise to a stirred solution of the Alk_2Mg compound cooled with an ice bath. The reaction mixture was worked up as described above. The yield of 3-ethyl-3-pentanol (Experiment 8.1) was determined as described for Experiments 7.1–7.3. 9-ethyl-9-heptadecanol was isolated with 99.7% purity (GC analysis) by distillation in high vaccum (bath temp. for both 130–160°C) and identified by IR, ^1H-NMR and mass spectra.

Table 8. Tertiary alcohols from Alk_2Mg compounds and ethyl propionate in a ca. 1.2 : 1 molar ratio in THF at room temp.

Expt. No.	Alk_2Mg comp. (mmol)	$EtCO_2Et$ [mmol]	React. time [h]	Reaction product (yield [%])
1	Et_2Mg (53)	44	1	Et_3COH (86)
2	Oct_2Mg (47)	38	16	Oct_2EtCOH (68)

Ketones from Oct_2Mg and Acyl Chlorides (Table 9): Except for Experiment 9.2, 1 M Oct_2Mg solutions (standardized experiment) were slowly added to cooled (Table 9) and stirred 0.2–0.3 M THF solutions of freshly distilled acyl chlorides and, in some cases (Table 9), of the $Fe(acac)_3$ catalyst. In the inverse addition mode (Experiment 9.2), a 1.6 M EtCOCl solution was added dropwise to the stirred 0.2 M Oct_2Mg solution. The reaction mixtures were hydrolyzed and neutralized with an aq. NH_4Cl solution (cooling with an ice bath) and extracted with several portions of ether. The combined ether extracts were washed with a sat. NaCl solution and dried with Na_2SO_4. The solvents and ketones were distilled in vacuo at room temp. and at elevated temp., respectively. From the elevated-temperature distillation, pure ketones were obtained or isolated from the distillates by preparative gas chromatography (see Table 9). The ketones were identified by GC or GC/MS analysis.

Pelargonic Acid from Oct_2Mg and CO_2: 25 ml of a 1.23 M Oct_2Mg solution, prepared according to the standardized Experiment (31 mmol), was diluted with 80 ml of THF, and dry CO_2 was passed through the solution cooled with an ice bath. The temp. of the reaction mixture increased to 30°C and after 10 min decreased. The reaction mixture was hydrolyzed by the addition of H_2O and 5 N HCl. After the addition of solid $MgCl_2$, the two phases were separated, and the organic layer was dried with Na_2SO_4. THF was

Table 9. Ketones from Oct_2Mg and acyl chlorides

Expt. No.	Oct_2Mg [mmol]	RCOCl (mmol)	$Fe(acac)_3$[a] [mol–%]	Addition of Oct_2Mg [°C]/[h]	Subsequent reaction[b] [°C]/[h]	Yield of OctCOR [%]
1	26	MeCOCl (50)	7	−10+15/2	r.t./2	57[c]
2[d]	34	EtCOCl (69)	–	−73/2[d]	−73/2[e]	71[c]
3	33	EtCOCl (69)	–	−73/1	−73/1 r.t./1	45[f]
4	27	EtCOCl (54)	6	−6+6/3	r.t./1	58[f]
5	30	PrCOCl (60)	3	−10+10/1	r.t./1	60[f]
6	26	PhCOCl 57)	–	−73/2	r.t/2	40[c]
7	25	PhCOCl (50)	4	−30−20/2	r.t./3	67[f]

[a] Related to RCOCl. — [b] r.t. = room temp. — [c] Yield based on GC analysis. — [d] Inverse mode of addition. — [e] The reaction mixture was subsequently warmed to room temp. — [f] The yields refer to pure products isolated by distillation or preparative gas chromatography and are based on starting acyl chlorides.

distilled off at normal pressure. The distillation of the residue in high vacuum (bath temp. 150−200°C) afforded 7.57 g (78%) of pelargonic acid which was identified by mass spectrometry.

Trimethyl-n-octylsilane from Oct_2Mg and Chlorotrimethylsilane: 10.0 ml of a 1.69 M Oct_2Mg solution prepared according to the standardized experiment (17 mmol) was diluted with 12 ml of THF. To this solution 4.3 ml (34 mmol) of chlorotrimethylsilane (CTMS) was added dropwise and with stirring over a period of 30 min. The maximum temp. rise during the CTMS addition was 35°C. The reaction mixture was then stirred at room temp. for 1 h and at 50°C for 1 h. Distillation of the mixture in vacuo (the distillate was cooled to −78°C) afforded 19.6 g of a liquid containing 28.9% of trimethyl-*n*-octylsilane and 0.09% of trimethylisooctylsilane (GC and GC-MS analysis; ratio of *n* to iso compound 99.7:0.3; yield 90%).

Tetra-n-butyltin from Bu_2Mg and $SnCl_4$: A solution of 3.00 ml (26 mmol) of $SnCl_4$ in 50 ml of heptane was added dropwise and with stirring to a solution of 49 ml (1.47 M) of Bu_2Mg prepared as in Experiment 3.1 (63 mmol). The mixture was heated for 2 h under reflux and then treated with 5 ml of H_2O and 20 ml of 10% HCl. The organic layer was separated and dried with $CaCl_2$. The solvents were distilled off in vacuo. The distillation of the residue in high vacuum afforded 7.71 g (83%) of tetra-*n*-butyltin (purity 96%, according to GC analysis) which was identified by mass spectrometry.

$C_{16}H_{36}Sn$ (347.2)

	C	H	Cl	Sn
Calcd.	55.35	10.45	0.00	34.19
Found	55.44	10.46	0.15	34.06

Tetra-n-octyltin from Pure Oct_2Mg and $SnCl_4$: A solution of 2.13 ml (18 mmol) of $SnCl_4$ in 50 ml of heptane was added dropwise over a period of 10 min to a stirred solution of 10.95 g (44 mmol) of Oct_2Mg, isolated in a pure form as described above, in 50 ml of THF. At the end of the $SnCl_4$ addition a white precipitate had formed, and the mixture was heated under reflux for $3\frac{1}{3}$ h and then worked up as described above for the preparation of tetra-*n*-butyltin. Yield: 9.94 g (95%; purity 99.1%, according to GC analysis). Tetra-*n*-octyltin was identified by mass spectrometry.

$C_{32}H_{68}Sn$ (571.6)

	C	H	Cl	Sn
Calcd.	67.24	11.99	0.00	20.77
Found	67.36	12.05	0.10	20.36

Tri-n-octylphosphane from Pure Oct_2Mg and PCl_3: A solution of 1.92 ml (22 mmol) of PCl_3 in 40 ml of heptane was added dropwise over a period of 2 h to a stirred solution of 10.36 g (41 mmol) of Oct_2Mg in 45 ml of THF (isolated in pure form as described above). During the PCl_3 addition, the temperature of the reaction mixture was increased to max. 45°C and the mixture was heated at reflux for 30 min. The solvents were distilled off in vacuo. The vacuum distillation of the residue (the fraction distilling up to 100°C was discarded) yielded 7.02 g (84%) of tri-*n*-octylphosphane (oily liquid with b.p. 150−200°C in high vacuum; purity 97.4%, according to GC analysis) which was identified by mass spectrometry.

Tri-n-octylphosphane from a Catalyst-Containing Oct_2Mg Solution and PCl_3: The preparation and isolation of tri-*n*-octylphosphane was carried out as described above, except that a catalyst-containing solution of Oct_2Mg prepared in accordance with the standard experiment was used: 2.00 ml (23 mmol) of PCl_3 in 20 ml of cyclohexane, 25.0 ml of a 1.68 M Oct_2Mg solution (42 mmol) diluted with 20 ml of THF. Yield: 7.50 g (85%; purity 96.3%, according to GC analysis) of tri-*n*-octylphosphane which was identified by mass spectrometry.

1-Octanol from Pure Oct_2Mg and Oxygen: A stream of dry oxygen diluted with argon was passed through a cooled and stirred solution of 1.37 g (5.5 mmol) Oct_2Mg (isolated in a pure form as described above) in 20 ml of toluene at such a rate that the temp. of the solution varied between 0 and +5°C. The reaction was considered to be complete, when a temp. increase was no longer observed in the presence of oxygen. The reaction mixture was hydrolyzed by the addition of 10 ml of 2 N H_2SO_4. The two phases were separated and the aqueous phase was extracted several times with toluene. The combined toluene phases were shaken with a $NaHCO_3$ solution and dried with $MgSO_4$. After removal of the solvent, 1-octanol was distilled in vacuo. Yield: 1.17 g (82%; purity 99.3%, according to GC analysis); the refractive index of the compound ($n_D^{21} = 1.4295$) was in agreement with that reported in the literature.

1-Octanol from a Catalyst-Containing Oct_2Mg Solution and Oxygen: 20.0 ml of a 0.98 M, catalyst-containing Oct_2Mg solution (standardized experiment; 19.5 mmol, calculated on the basis of a GC analysis of *n*-octane obtained by hydrolysis of Oct_2Mg) was diluted with 20 ml of THF. The reaction flask was evacuated and with stirring and cooling (ice cold water) dry oxygen from a gas burette was carefully (exothermic reaction!) introduced into the flask at such a rate that the maximum temp. attained was 30°C. The solution was saturated by absorption of 530 ml of O_2 (20°C/1 bar), hydrolyzed as well as neutralized with 5 N HCl. The organic layer was then separated and extracted several times with toluene. Then the combined extracts were distilled in vacuo to afford 4.66 g (91%) of *n*-octanol containing 0.3% of isooctanol (GC analysis).

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