

According to the X-ray structure analysis^[4] (1) is a dimer (Fig. 1) with symmetry $\bar{1}$ (C_i). The oxygen atoms of the symmetry-related benzophenone moieties (O1, O1') are bridged by a metal-metal contact of bonding dimensions (Li1—Li1': 2.452(10) Å)^[5] (see Fig. 2). The Li—O distances within this planar four-membered ring are equal (1.867(8) Å); the dihedral angle between the planar four-membered ring and the plane of the benzophenone moiety (O1C1C2C8) is 110.4°. Hence both lithium atoms (Li1, Li1') of this metal-metal system interact with one lone pair of the carbonyl oxygen (three-center bonding), while the other lone pair is directed towards one of the "unique" lithium atoms (Li2). The latter, however, has an additional ion-pair interaction with the central planar part of the carbon skeleton of the benzophenone (C1, C2, C7) (dihedral angles O1C1C2C7: 2.7°, O1C1C8C13: 23.5°). Bonds of this type, with similar lengths, also exist in benzyllithium^[6] or triphenylmethyl lithium^[7]. As expected Li1—O2 (1.919(8) Å) is shorter than Li—C (2.21—

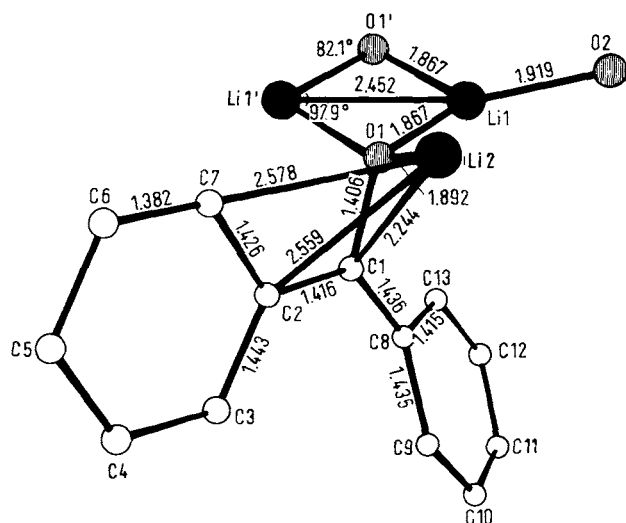


Fig. 2. Principal bond lengths [Å] and angles in (1) (substructure).

2.54). Two coordination sites on the almost tetrahedral Li2 are occupied by the nitrogen atoms of one TMEDA molecule, while a slightly angularly oriented THF molecule occupies a free site at Li1 and at Li1'.

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(1), 75112-28-6

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- [4] Crystallographic data: $a = 9.769(2)$, $b = 11.297(2)$, $c = 11.913(2)$ Å, $\alpha = 110.27(2)$, $\beta = 104.98(1)$, $\gamma = 92.67(2)^\circ$; space group $P\bar{1}$, $Z = 1$, $\rho_{\text{calc}} = 1.084$ g cm⁻³; 2680 reflections, of which 1812 observed; $R = 0.058$.
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Catalytic Synthesis of Magnesium Hydride under Mild Conditions

By Borislav Bogdanović, Shih-tsen Liao, Manfred Schwickardi, Peter Sikorsky, and Bernd Spliethoff^[*]

The direct synthesis of magnesium hydride from the elements requires extremely long reaction times and drastic conditions^[1]. Since hydrides of magnesium and its alloys and hydrides of intermetallic magnesium compounds are of potential use in reversible hydrogen storage devices^[2], great efforts have already been directed at improving the hydrogenation of magnesium by addition of foreign metals or by alloying^[1e, 2, 3]. In contrast, little is known about the use of homogeneous transition-metal catalysis for the hydrogenation of magnesium^{[4][***]}. We report here on such a synthesis, which for the first time affords highly reactive magnesium hydride under mild conditions and which can also be carried out on a large scale.

Combinations of organic compounds of the main group elements with transition metal halides serve as suitable catalysts, which if necessary are activated by polycyclic arenes or amines; particularly active catalysts are obtained by reaction of anthracenemagnesium^[5] with chromium, titanium, or iron halides in tetrahydrofuran (THF)^[6]. Olive-green (Cr, Fe) or violet (Ti) THF solutions are formed, which already catalyze the hydrogenation of magnesium over days at 20 °C and normal pressure. To increase the rate of hydrogenation the catalysis can be carried out at 40–70 °C under H₂-pressure. As shown for the chromium catalyst (Fig. 1), for example, with this method and with a molar ratio of Mg:catalyst of 100:1 or 200:1, magnesium can be converted quantitatively into magnesium hydride within ca. 10 or 16 h, respectively, at 60–70 °C/80 bar.

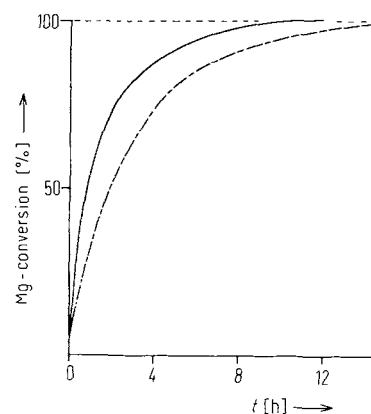


Fig. 1. Hydrogenation of magnesium with an anthracenemagnesium/CrCl₃ catalyst at 60–70 °C/80 bar; (—) Mg:Cr = 100:1, [Cr] = 0.086 mol/l; (---) Mg:Cr = 200:1, [Cr] = 0.043 mol/l.

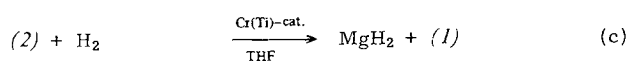
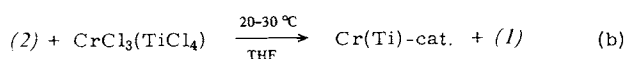
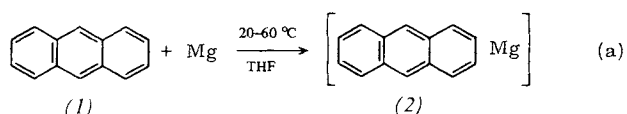
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[***] In US-Pat. 3 167 218 (E. van Tamelen, R. Fechter, 1968) the production of alkali metal hydrides from the metals and hydrogen in the presence of, e.g. naphthalene and titanium tetraisopropylate is claimed, but only that of sodium hydride is described as example (as also in the later publication *J. Am. Chem. Soc.* 90, 6854 (1968)). In the general description also the possibility of the hydrogenation of the alkaline earth metals and of aluminum is mentioned, as well as a series of further catalyst combinations. According to our own experiments, however, the catalysts recommended therein are unsuitable for the hydrogenation of alkaline earth metals and aluminum.

According to preliminary kinetic measurements the rate of hydrogenation is nearly proportional to the concentration of chromium or titanium catalyst and corresponds to a reaction of first order referred to magnesium^[7]. In the case of the chromium catalyst (0.086 mol Cr/l) the rate of hydrogenation increases only slightly with increasing hydrogen pressure between 5 and 80 bar.

The following experimentally verified reactions may be regarded as possible steps of the homogeneously catalyzed hydrogenation of magnesium: (i) metallic magnesium reacts with anthracene in THF at 20 °C or above in the molar ratio 1:1 to give orange, sparingly soluble anthracenemagnesium (2) [eq. (a)]; (ii) in the reaction of (2) with CrCl₃ or TiCl₄ in THF, which leads to formation of the catalytically active species, free anthracene (1) is formed [eq. (b)]; (iii) in presence of the dissolved chromium or titanium catalyst, (2) is hydrogenated by hydrogen (at 30–60 °C/80 bar) to magnesium hydride [eq. (c)], with liberation of anthracene (1) (only small amounts of 9,10-dihydroanthracene were detected).



The reaction sequence eq. (a) and eq. (c) represents a catalytic cycle of magnesium hydrogenation *via* anthracenemagnesium (2) as intermediate. This assumption is supported by the experimental finding that the hydrogenation of (2) [eq. (c)] according to our method is considerably faster than the hydrogenation of elemental magnesium.

Thus, in this method a magnesium hydride/magnesium system is obtained which, because of the high dehydrogenation/hydrogenation rate (at 200–350 °C/1–50 bar) and high content of reversibly bound hydrogen in the magnesium hydride so produced (*ca.* 7 wt-%), is particularly suitable as a hydrogen storage system.

Procedure

All reactions carried out under argon. A suspension of magnesium powder (73.2 g, 3.0 mol) (Riedel-de Haën) in anhydrous THF (350 ml) is treated with ethyl bromide (0.3 ml) and, after 30 minutes' stirring, with 5.35 g (30.0 mmol) of (1). After three hours' stirring (during which time (2) is formed) anhydrous CrCl₃ (4.75 g, 30.0 mmol) is added and stirring continued for a further 15–30 min until cessation of the weakly exothermic reaction. The olive-green suspension is transferred to a 1 l autoclave fitted with glass insert and magnetic stirrer and hydrogenated at 60–65 °C external temperature and a H₂-pressure of 80 bar; the rate of hydrogenation (Fig. 1) is measured *via* the drop in pressure in a hydrogen storage vessel. On completion of reaction the light-gray suspension is filtered through a glass frit (D4, diameter 9 cm)^[8], and the MgH₂ washed twice with THF and pentane and dried in a high vacuum at 20 °C. One obtains 76.0 g of a pyrophoric magnesium hydride which is free from elemental magnesium; according to the elemental analysis and the amount of hydrogen liberated by hydrolysis the MgH₂ is *ca.* 94% pure (rest: THF, MgCl₂, catalyst^[9]).

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- [7] The kinetic measurements were carried out in a 2 l autoclave fitted with stirrer.
- [8] The filtration is laborious; a much quicker filtration, particularly in experiments on a larger scale (up to 0.7 kg Mg), is possible with a pressure filter (Polypropylene cloth 2832, Verseidag).
- [9] The procedure for the production of MgH₂ with TiCl₄ or FeCl₂ is analogous; the product is somewhat coarser and more easily filterable.

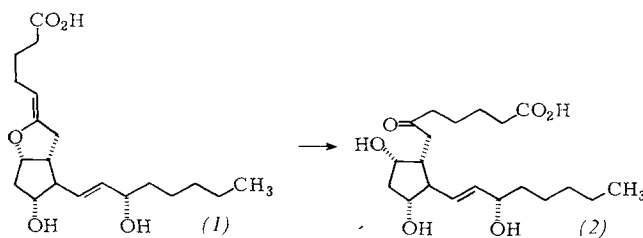
New Prostacyclin Analogues

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Dedicated to Professor Rolf Huisgen on the occasion of his 60th birthday

Prostacyclin (PGI₂) (1)^[1] has been found in animal and human experiments to lower the blood pressure and to hinder platelet aggregation after intravenous administration^[2]. Since it is less rapidly biologically deactivated than the "classical" prostaglandins E₂ and F_{2α} it has been considered as a circulating hormone affecting the circulation^[3].

Aqueous solutions of pure (1) have a half-life of only 3 min at pH 7.5 and 37 °C^[4]; (1) is hydrolyzed to 6-oxo-PGF_{1α} (2).



It has been a preparative goal of various laboratories to synthesize chemically more stable analogues of (1)^[5]. As far as can be seen, the biological action of (1) is closely connected with the electronic and steric parameters of the enol ether structure. Prostacyclin analogues differing considerably from the natural product in this partial structure are biologically less active^[6].

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