

Magnesium Anthracene Systems and Their Application in Synthesis and Catalysis[†]

BORISLAV BOGDANOVIĆ

Max-Planck-Institut für Kohlenforschung, 4330 Mülheim a.d. Ruhr 1, FRG

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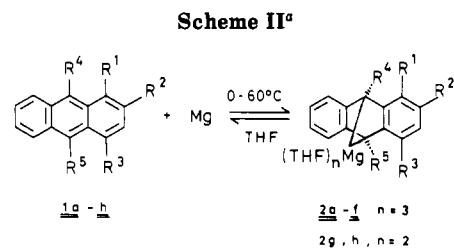
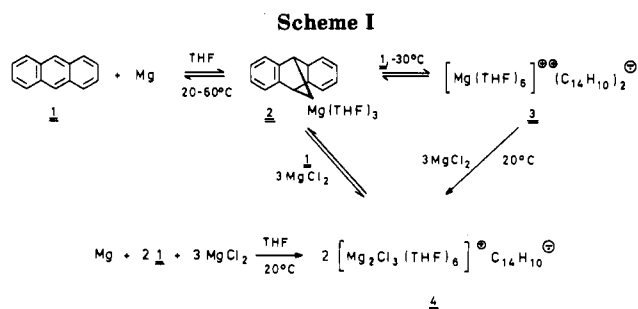
Although the reaction of magnesium with anthracene in THF to form the orange, sparingly soluble magnesium anthracene was discovered by Ramsden in 1965,¹ the chemistry of magnesium anthracene systems began to develop only in the 1980s, triggered by the application of magnesium anthracene to generate a catalyst system for the hydrogenation of magnesium under mild conditions.² Nowadays, magnesium anthracene compounds attract broad interest because of their versatile applications in synthesis and their ability to catalyze reactions of metallic magnesium. Elemental magnesium in the presence of a catalytic amount of anthracene can be hydrogenated to a highly reactive form of magnesium hydride, is an excellent reducing agent for transition-metal salts, and can be used to prepare Grignard compounds under extremely mild conditions. The active MgH_2 -Mg system, accessible via phase-transfer catalysis of magnesium, can be applied for chemical syntheses and is an outstanding medium for hydrogen and high-temperature heat storage. An account of these topics, emphasizing recent synthetic and catalytic applications, will be given here.³

Magnesium Anthracene Systems: Preparation, Properties, and Structure

Magnesium anthracene, $MgC_{14}H_{10} \cdot 3THF$ (**2**),⁴ is prepared in high yield by reacting magnesium with anthracene (**1**) in THF in the absence of air and moisture.⁵ Upon protolysis of **2** 9,10-dihydroanthracene is formed quantitatively.⁴ The complexed THF in **2** can be displaced by other mono-, bi-, or tridentate ligands L such as 1,4-dioxane, DME, ethylbis-(2-methoxyethyl)amine, PMDTA, and 1,4,7-trimethyl-1,4,7-triazacyclononane, yielding poorly soluble pentacoordinate complexes $C_{11}H_{10}Mg \cdot L_n$.⁶⁻⁸

The rate of formation of **2** depends both on the magnesium surface area and on the anthracene concentration. According to kinetic measurements, between **2** and **1**, Mg, and THF exists a reversible, temperature-dependent equilibrium, **2** being favored at lower temperatures.⁴ Thus, either by decreasing the concentration of THF and/or **1** in the system or by raising the temperature, one can shift the equilibrium $Mg + 1 \rightleftharpoons 2$ (Scheme I) from right to left, which is a method for generating elemental magnesium in a finely dispersed active form (Mg^* ; vide infra).

Borislav Bogdanović was born and educated in Yugoslavia. He studied chemistry and acquired the first degree (diploma) at the University of Belgrade in 1959 and his doctoral degree in 1962 (with G. Wilke) from the Technical High School Aachen. In 1960 he joined the Max-Planck-Institut für Kohlenforschung in Mülheim (Ruhr), West Germany, where he is now the head of a department. Since 1974 he has been lecturer and in 1976 was appointed Professor at the Ruhr-Universität (Bochum). His research interests include organometallic chemistry and the application of catalysis to organic and inorganic synthesis. In recent years he has become involved in the problems of energy storage using the MgH_2 -Mg system.



^a R = H if not noted otherwise. a, R² = CH₃; b, R¹, R³ = CH₃; c, R⁴ = CH₃; d, R⁴ = C₂H₅; e, R⁴, R⁵ = CH₃; f, R⁴ = C₆H₅; g, R⁴ = (CH₃)₃Si; h, R⁴, R⁵ = (CH₃)₃Si.

The low thermal stability of **2** is plausible in view of the molecular structure of the related magnesium 1,4-dimethylantracene·3THF⁹ (**2b**, Figure 1). The magnesium atom in **2b** is pentacoordinate, exhibiting unusually long Mg-C bonds (2.32 Å) and a sharp C₉-Mg-C₁₀ bond angle (72.6°), with the anthracene moiety being folded along the C₉-C₁₀ line (40.95°) owing to the loss of aromaticity of the central ring. On the basis of the nearly identical ¹³C NMR spectra of both compounds, a monomeric **2** with the same structural elements as those found for **2b** has been assumed⁹ and recently confirmed by X-ray analysis.¹⁰

[†] Abbreviations: THF, tetrahydrofuran; TMEDA, tetramethylethylenediamine; PMDTA, pentamethyldiethylenetriamine; DME, 1,2-dimethoxyethane; DABCO, diazabicyclooctane; Cp, η⁵-cyclopentadienyl group; COD, 1,5-cyclooctadiene; Pe, pentane; acac, acetylacetonate group; Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl.

(1) Ramsden, H. E. U.S. Patent 3 354 190, 1967; *Chem. Abstr.* 1968, 68, 114744.

(2) (a) Bogdanović, B.; Liao, S.; Schwickardi, M.; Sikorsky, P.; Spliethoff, B. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 818. (b) Bogdanović, B. Eur. Patent 3564, 1982; *Chem. Abstr.* 1979, 91, 159787; U.S. Patent 4554 153, 1985.

(3) Previous reviews: Bogdanović, B. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 262. Bogdanović, B. In *Organic Synthesis: An Interdisciplinary Challenge*; Streith, J., Prinzbach, H., Schill, G., Eds.; Blackwell: Oxford, 1985; p 63.

(4) Bogdanović, B.; Liao, S.; Mynott, R.; Schlichte, K.; Westeppe, U. *Chem. Ber.* 1984, 117, 1378.

(5) Bogdanović, B.; Liao, S.; Schlichte, K.; Westeppe, U. *Organomet. Synth.*, Vol. 4, accepted for publication.

(6) (a) Alonso, T.; Harvey, S.; Junk, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *Organometallics* 1987, 6, 2110. (b) Bogdanović, B.; Janke, N.; Kinzelmann, H.-G.; Westeppe, U. *Chem. Ber.* 1988, 121, 33.

(7) Westeppe, U. Dissertation, University of Bochum, 1985.

(8) Janke, N. Dissertation, University of Bochum, 1986.

(9) Bogdanović, B.; Janke, N.; Krüger, C.; Mynott, R.; Schlichte, K.; Westeppe, U. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 960.

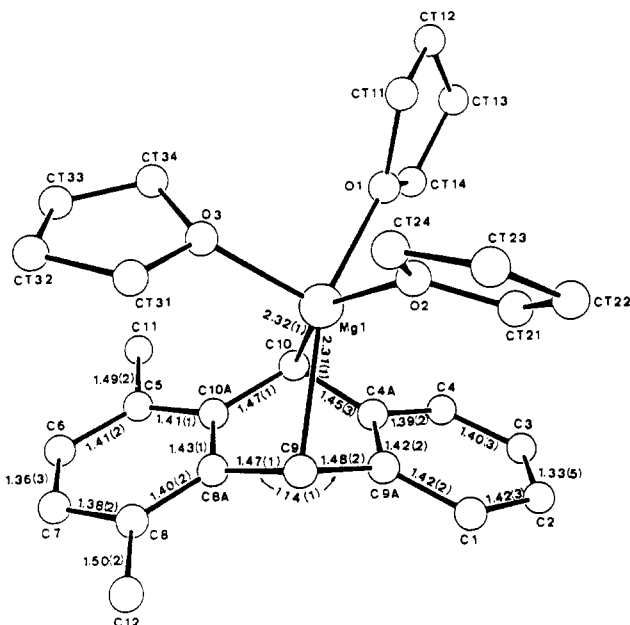


Figure 1. Molecular structure of **2b**. Reprinted with permission from ref 9; copyright 1985 VCH Publishers, Inc.

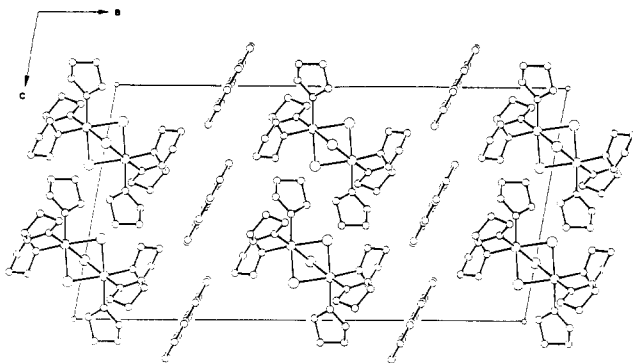
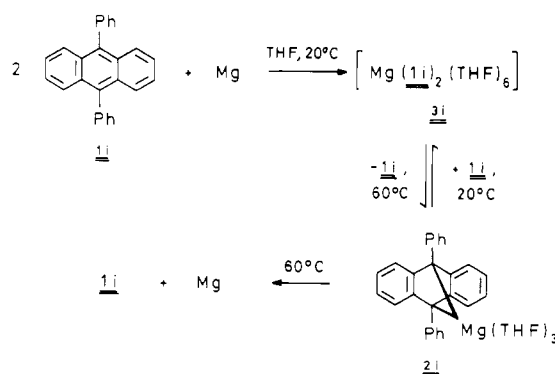


Figure 2. Molecular structure of **4**. Reprinted with permission from ref 9; copyright 1985 VCH Publishers, Inc.

At $-30\text{ }^\circ\text{C}$ in THF, **2** transfers an electron to **1** to form the blue insoluble magnesium bis(anthracenide)·6THF (**3**), which, after addition of MgCl_2 , affords the blue crystalline radical anion complex $[\text{Mg}_2\text{Cl}_3(\text{THF})_6]^+\text{C}_{14}\text{H}_{10}^{\cdot-}$ (**4**) at room temperature.⁹ **4** is also produced by reaction of **2**, **1**, and MgCl_2 or Mg , **1**, and MgCl_2 in THF. The equilibrium between **4** and **1**, **2**, and MgCl_2 in THF depends on both temperature and concentration of MgCl_2 . The crystal structure of **4** (Figure 2) displays, for the first time, an example of an anthracene radical anion as a distinct species of a solvent-separated ion pair. The bond lengths and the electron deformation density of the anthracene radical anion show unequivocally that in **4** the LUMO is occupied by one electron.⁹ The rapid temperature-dependent equilibrium between magnesium, anthracene, MgCl_2 , and the highly reactive soluble organometallic species **2**, **3**, and **4** in THF (Scheme I) is the basis for the phase-transfer catalytic activity for elemental magnesium of the magnesium anthracene- MgCl_2 -THF system described later.

Alkyl- (**1a-e**),^{8,11} 9-phenyl- (**1f**),^{8,11} and trimethylsilyl-substituted anthracenes (**1g,h**)¹² react with mag-

Scheme III



nesium in THF as well to yield the corresponding magnesium anthracene adducts **2a-h** (Scheme II). The crystalline, yellow, orange, or brown compounds **2a-h** are characterized by ^1H and ^{13}C NMR spectra, by hydrolysis to the corresponding 9,10-dihydroanthracenes, and in the case of **2b** (Figure 1)^{8,9} and **2h**,¹² also by X-ray analysis. **2a-c,e,f,i**, also exhibit temperature-dependent equilibria with **1a-h** and Mg in THF. As compared to the equilibrium for **2**,⁴ these equilibria are strongly shifted toward the starting materials, and only at $0\text{ }^\circ\text{C}$ are high conversions achieved.^{8,11}

In contrast to anthracene and substituted anthracenes **1a-h** (Scheme II), 9,10-diphenylanthracene (**1i**) reacts with magnesium powder in THF at $20\text{ }^\circ\text{C}$ to yield the deep blue magnesium bis(9,10-diphenylanthracenide)·6THF (**3i**) (Scheme III). The color and protolysis of **3i** affording a 1:1 mixture of **1i** and 9,10-diphenyl-9,10-dihydroanthracene suggest the presence of the 9,10-diphenylanthracene radical anion,¹³ i.e., **3i** is a homologue of **3**. Upon heating to $60\text{ }^\circ\text{C}$ in THF, **3i** reversibly dissociates to **2i** and free **1i**, while prolonged heating at $60\text{ }^\circ\text{C}$ leads to the decomposition of **2i** to magnesium and **1i**.^{8,11}

Stoichiometric Reactions of 2

Of the magnesium anthracene compounds **2**, **2a-i**, **3**, **3i**, and **4**, only the reactivity of the parent compound **2** has been thoroughly investigated up to now. Owing to its easy accessibility and versatile reactivity, **2** has become a useful novel organometallic reagent for a number of stoichiometric and catalytic applications. **2** can be described as an ambivalent species that can react as a diorganomagnesium compound (or as a nucleophile), as "a source of soluble zerovalent magnesium", and as a single-electron donor. The high reactivity and the tendency of **2** for homolytic rather than heterolytic Mg-C bond cleavage can be explained by the weakness of its Mg-C bonds, and the ability of **2** to act as a single-electron donor can be explained by the ease with which **2** is transformed to radical anion species such as **3** and **4** (Scheme I).

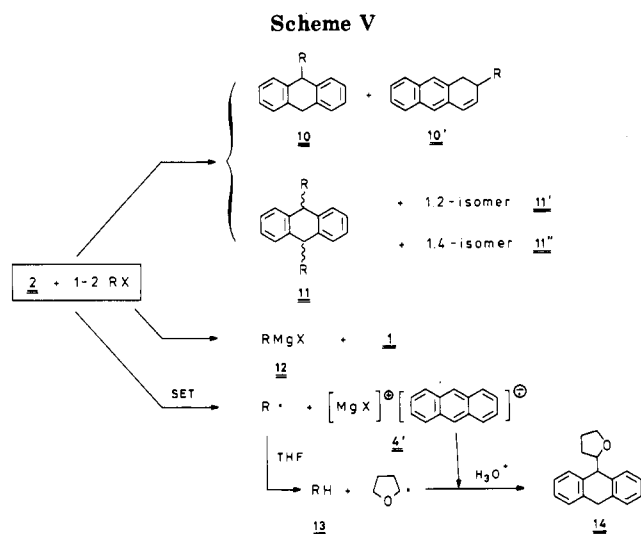
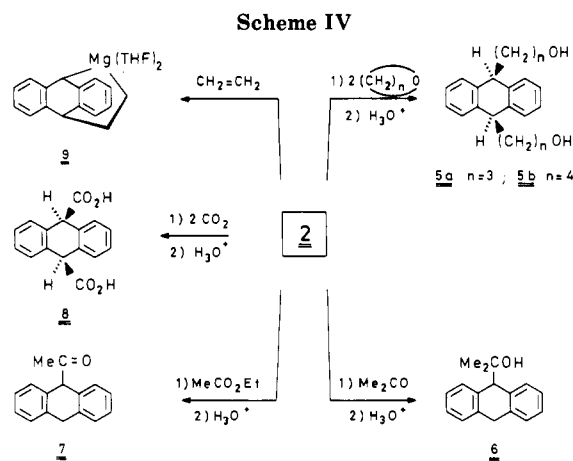
Toward oxygen-containing organic compounds and ethene, **2** behaves like a normal diorganomagnesium compound, although in some cases only one Mg-C bond can be synthetically utilized. At $130\text{ }^\circ\text{C}$ under pressure both Mg-C bonds in **2** are cleaved by THF, yielding, after protolysis, 9,10-bis(4-hydroxybutyl)-9,10-di-

(12) Lehmkuhl, H.; Shakoor, A.; Mehler, K.; Krüger, C.; Angermund, K.; Tsay, Y.-H. *Chem. Ber.* **1985**, *118*, 4239.

(13) Wheeler, L. O.; Santhanam, K. S. V.; Bard, A. J. *J. Phys. Chem.* **1966**, *70*, 404.

(10) Engelhardt, L. M.; Harvey, S.; Raston, C. L.; White, A. H. *J. Organomet. Chem.* **1988**, *341*, 39.

(11) Bogdanović, B.; Janke, N., in preparation.



hydroanthracene (**5a**),⁴ while the analogous reaction with oxetane takes place even at 0 °C to give diol **5b** (Scheme IV). The reactions with acetone and ethyl acetate lead primarily to tertiary alcohol **6** and ketone **7**, respectively, while carboxylation yields *cis*-9,10-dihydroanthracene-9,10-dicarboxylic acid (**8**).⁸

The insertion of ethene into the Mg-C bonds of allyl-, *sec*-alkyl, *tert*-alkyl-, and benzylmagnesium halides has been investigated by Lehmkuhl et al.¹⁴ In THF under pressure, **2** reacts likewise with ethene by insertion into one of the Mg-C bonds, yielding crystalline 9,10-(1-magnesiopropano)-9,10-dihydroanthracene-2THF (**9**). The bicyclic monomeric structure of **9** has been confirmed by X-ray spectroscopy.¹⁵ **9** behaves as a typical diorganomagnesium compound, except that it shows a higher reactivity of the secondary (long, 2.21 Å) than the primary (short, 2.11 Å) Mg-C bond.¹⁵

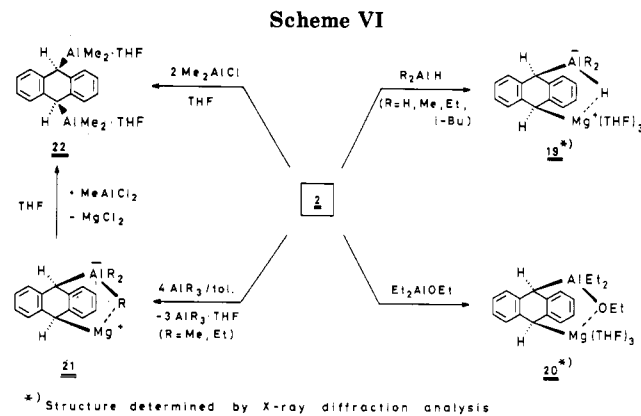
With organic halides, **2** can react in three different ways, depending on the substrate (Scheme V): as a nucleophile, yielding mono- and disubstituted dihydroanthracenes (**10**, **10'**, **11**-**11''**), as a source of zerovalent magnesium to produce Grignard compounds (**12**) and anthracene (**1**), and as a single-electron donor with reduction of the halide to RH (**13**) and formation of the tetrahydrofuran derivative **14**.^{8,16-18} With pri-

(14) Review: Lehmkuhl, H. *Bull. Soc. Chim. Fr.* 1981, II-87.

(15) Bogdanović, B.; Janke, N.; Krüger, C.; Schlichte, K.; Treber, J. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 1025.

(16) Bogdanović, B. *Ger. Offen.* DE 3340492, 1985; *Chem. Abstr.* 1985, 103, 196226; U.S. Patent 4659373, 1987.

(17) Bogdanović, B.; Janke, N.; Kinzelmann, H.-G.; Treber, J., in preparation.

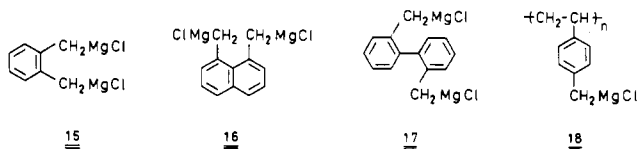


mary and secondary alkyl halides in THF, the major products are **11**-**11''**, and with *tert*-butyl halides, the major products are **10** and **10'**.^{8,17}

A single-electron transfer¹⁹ appears to be the major pathway for reaction of **2** with bromo- or iodobenzene in THF since benzene and **13** are the major products. In the first step of this reaction, probably the phenyl radical and complex **4'** (corresponding to **4**) are formed. The abstraction of a hydrogen atom from the solvent by the phenyl radical leads to benzene, while the resulting 2-tetrahydrofuran radical recombines with the anthracene radical anion from **4'** to give, after protolysis, **14**.^{8,17}

In contrast to alkyl halides, allyl, propargyl, and benzyl halides can be used to prepare Grignard compounds from **2** in toluene, ether, and THF.^{8,16,17,20} The generation of allyl type Grignard compounds (Scheme V, **12**, R = allyl or substituted allyl) from allyl, methallyl, and crotyl chlorides and **2** in THF is possible at temperatures as low as -78 °C.^{8,16,17} A notable example of the advantage offered by this novel method is the synthesis of allenylmagnesium chloride **12** (R = CH₂=C=CH) from propargyl chloride and **2** in THF.¹⁷ Propargyl chloride does not react with either ordinary²¹ or activated magnesium.¹⁷ The generation of allyl and allenyl type Grignard compounds can be carried out with catalytic amounts of **2** as well.

Benzyl chloride reacts with **2** in THF, ether, and benzene to produce benzylmagnesium chloride and **1**.^{8,17} Bifunctional benzyl type Grignard compounds **15**-**17**



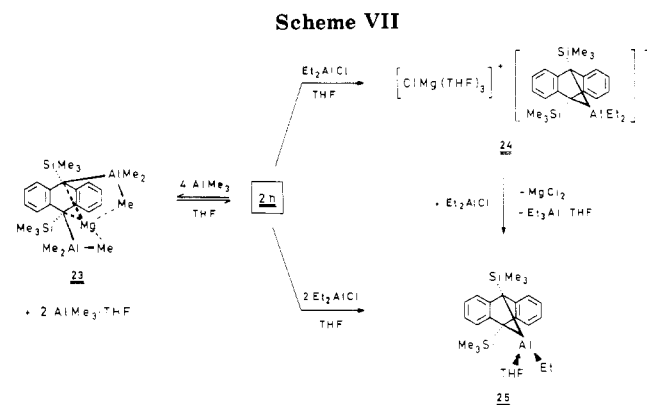
have been prepared accordingly, in high yields, from the corresponding benzyl chlorides and **2** in THF.²⁰ A remarkable recent achievement in this field is the first direct synthesis of a polymeric Grignard compound **18** from *p*-(chloromethyl)polystyrene and **2**.²²

(18) Bogdanović, B.; Schlichte, K.; Westeppe, U. *Chem. Ber.* 1988, 121, 27.

(19) Reviews: Dagonneau, M. *Bull. Soc. Chim. Fr.* 1982, II-269. Holm, T. *Acta Chem. Scand., Ser. B* 1983, 37, 567.

(20) (a) Raston, C. L.; Salem, G. *J. Chem. Soc., Chem. Commun.* 1984, 1702. (b) Engelhardt, L. M.; Papasergio, R. I.; Raston, C. L.; Salem, G.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1986, 789. (c) Gallagher, M. J.; Harvey, S.; Raston, C. L.; Sue, R. E. *J. Chem. Soc., Chem. Commun.* 1988, 289.

(21) (a) Newman, M. S.; Wotiz, J. H. *J. Am. Chem. Soc.* 1949, 71, 1292. (b) Jacobs, T. L.; Moore, T. L. *Abstracts of Papers*, 114th National Meeting of the American Chemical Society; American Chemical Society: Washington, DC, 1962; p 19-O.



The versatile reactivity of **2** is exhibited in particular in its reactions with metal or organometal halides and hydrides. **2** reacts with R_2AlH ($\text{R} = \text{H}$, alkyl) and $\text{Et}_2(\text{EtO})\text{Al}$ in THF to produce the complexes **19** and **20** (Scheme VI), respectively, in which Al and Mg occupy axial positions in a 9,10-dihydro-9,10-anthrylene system and Mg interacts respectively with the hydride or the alkoxide of the aluminate anion.^{23–25} The analogous triakylaluminum complexes **21** can be obtained when **2** is treated with excess of AlR_3 in a non Lewis base solvent.²³ **2** reacts with MeAlCl_2 to form 9,10-bis(dimethylaluminio)-9,10-dihydroanthracene·2THF (**22**), which is also accessible from **21** and MeAlCl_2 .^{24,25}

In contrast to **2**, **2h** reacts with Me_3Al to produce an insoluble 1:2 complex **23**, for which the structure shown in Scheme VII has been proposed.²⁴ **2h** and Et_2AlCl form an ionic 1:1 complex **24**, which upon further addition of Et_2AlCl gives **25**; direct reaction of **2h** and Et_2AlCl also produces **25**. The structure of **25** has been confirmed by X-ray spectroscopy.^{24,25}

Compounds with silicon²⁶ and tin¹ bridging the 9,10-positions of anthracene **26** (Scheme VIII) have been prepared from **2** and diorganosilicon and -tin dihalides. The reaction of **2** with dicyclopentadienyltitanium or -zirconium dichlorides, however, leads to the derivatives of divalent titanium and zirconium **27**, to which the η^4 -structure has been assigned.²⁷ With trimethylchlorosilane **2** reacts as a nucleophile to give mainly 9,10-bis(trimethylsilyl)-9,10-dihydroanthracene (**28**); the reaction with tri-*n*-butylchlorostannane, however, takes place with homolysis of the Mg–C bonds in **2**, affording hexabutylditin (**29**), anthracene, and MgCl_2 .⁷

Of particular importance is the reaction of **2** with TiCl_4 or CrCl_3 in THF in the presence of an excess of metallic magnesium, since the resulting dark-colored solutions **30** are used routinely as “homogeneous” catalysts (no precipitation of elemental Ti or Cr is observed) for the hydrogenation of magnesium to magnesium hydride and HMgCl (vide infra) and have also been used in the polymerization of acetylene.²⁸ The

(22) Itsuno, S.; Darling, G. D.; Stöver, H. D. H.; Fréchet, J. M. J. *J. Org. Chem.* **1987**, *52*, 4644.

(23) Lehmkuhl, H.; Mehler, K.; Benn, R.; Rufinska, A.; Schroth, G.; Krüger, C. *Chem. Ber.* **1984**, *117*, 389.

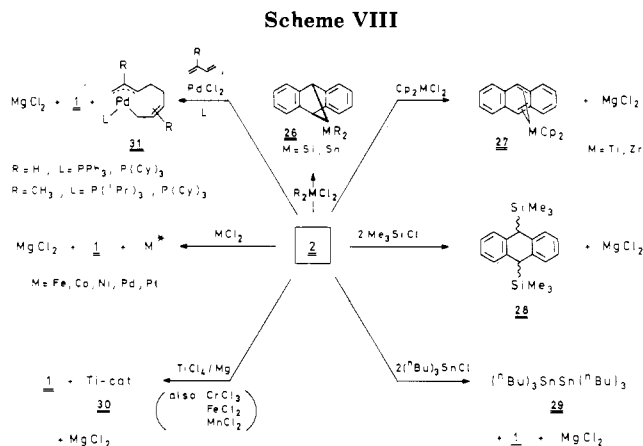
(24) Lehmkuhl, H.; Mehler, K.; Shakoar, A.; Krüger, C.; Tsay, Y.-H.; Benn, R.; Rufinska, A.; Schroth, G. *Chem. Ber.* **1985**, *118*, 4248.

(25) Lehmkuhl, H.; Shakoar, A.; Mehler, K.; Krüger, C.; Tsay, Y.-H. *Z. Naturforsch., B* **1985**, *40b*, 1504.

(26) Appler, H.; Gross, L. W.; Mayer, B.; Neumann, W. P. *J. Organomet. Chem.* **1985**, *291*, 9.

(27) Scholz, J.; Thiele, K.-H. *J. Organomet. Chem.* **1986**, *314*, 7.

(28) Yu, S.; Liao, S.; Yu, C.; Guo, H. *Cuihua Xuebao* **1986**, *7*, 183; *Chem. Abstr.* **1986**, *105*, 115469.

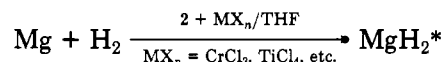


group VIII transition-metal chlorides can be reduced by **2** in THF to finely divided metal powder (M^*).²⁹ **2** has also been employed as a reducing agent for PdCl_2 in the synthesis of η^1, η^3 -octadienediyl complexes **31**, which proceeds in the presence of butadiene or isoprene and phosphanes.³⁰

Magnesium Anthracene–THF Systems as Phase-Transfer Catalysts for Magnesium³¹

The property of **2** to act as a source of soluble zero-valent magnesium under liberation of anthracene, which in the presence of magnesium in THF will regenerate **2**, can be utilized to catalyze reactions of metallic magnesium. As such reactions have been investigated the hydrogenation of magnesium in the presence of transition-metal catalysts, the reduction of metal salts by elemental magnesium in the presence or absence of electron donors, and the generation of allyl and allenyl Grignard compounds. For the purpose of the catalytically activating magnesium, **2** can be conveniently prepared in situ in the presence of excess magnesium. Ultrasound treatment of the system improves the efficiency of the catalytic reactions.^{16,29,32–35}

Catalytic Synthesis and Applications of Magnesium Hydride. The catalytic activation of magnesium via the magnesium anthracene species of Scheme I, for use in the synthesis of magnesium hydrides, has been extensively investigated.^{2,3,36} The catalyst system used to hydrogenate magnesium powder to magnesium hydride was originally prepared by reacting **2** with CrCl_3 or TiCl_4 in the presence of excess magnesium.



(29) Bogdanović, B.; Bönemann, H. Ger. Offen. DE 3 541 633, 1987; U.S. Patent 4 713 110, 1987.

(30) Benn, R.; Jolly, P. W.; Mynott, R.; Raspel, B.; Schenker, G.; Schick, K.-P.; Schroth, G. *Organometallics* **1985**, *4*, 1945.

(31) According to Starks: “The general concept of phase-transfer catalysis applies to the transfer of any species from one phase to another (not just anions...), provided a suitable catalyst can be chosen, and provided suitable phase compositions and reaction conditions are used”. Starks, C. M. In *Phase Transfer Catalysis*; Starks, C. M., Ed.; ACS Symp. Ser. 326; American Chemical Society: Washington, DC, 1987; p 2.

(32) Bönemann, H.; Bogdanović, B.; Brinkmann, R.; He, D.-W.; Spliethoff, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 728.

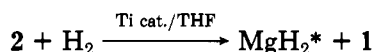
(33) Bönemann, H.; Bogdanović, B. U.S. Patents 4 469 638 (1984) and 4 556 719 (1985).

(34) Oppolzer, W.; Schneider, P. *Tetrahedron Lett.* **1984**, *25*, 3305.

(35) Oppolzer, W.; Cunningham, A. F. *Tetrahedron Lett.* **1986**, *27*, 5467.

(36) Bogdanović, B.; Spliethoff, B. *Hydrogen Energy Progress VI* (Proceedings of the 6th World Hydrogen Energy Conference, Vienna, 1986), Vol. 2, p 797; *Int. J. Hydrogen Energy* **1987**, *12*, 863.

The following reactions have been proposed to be involved in the hydrogenation reaction:² (i) the equilibrium between 1, magnesium, THF, and 2 (Scheme I); (ii) the reduction of TiCl₄ or CrCl₃ with 2 and excess magnesium to form MgCl₂ and 1 (Scheme VIII); and (iii) rapid hydrogenation of 2 in the presence of reduced Ti or Cr species, leading to MgH₂ and 1. (In the absence of the transition-metal catalyst, only a slow

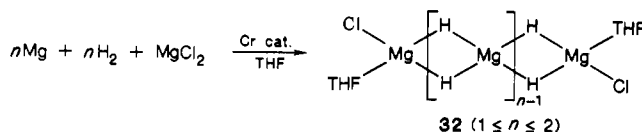


hydrogenation of 2 with concurrent formation of magnesium hydride and 9,10-dihydroanthracene takes place.³)

The combination of the first and the third of the above reactions represents the catalytic cycle of magnesium hydrogenation via the reactive intermediate 2.

Subsequently, the catalyst system for the hydrogenation of magnesium has been improved by adding MgCl₂ as a cocatalyst,^{7,37} thus reducing the time required for the quantitative hydrogenation of magnesium from 16–20 h to 1–2 h or less. It has been shown experimentally that the rate of formation of 2 and/or 4 in a system containing 1, Mg, and MgCl₂ (Scheme I) increases with increasing MgCl₂ concentration. The increased rate of magnesium hydrogenation in the presence of MgCl₂ can be explained by additional involvement of the radical anion species 4 in the process of the activation/dissolution of magnesium.⁷ (In the original process² only a small amount of MgCl₂ is formed in the course of the reduction of Ti or Cr chlorides (Scheme VIII).)

When, on the other hand, the catalytic hydrogenation of magnesium is carried out in the presence of stoichiometric amounts of MgCl₂ at 0 °C, the THF-soluble hydromagnesium chloride 32 can be obtained in nearly quantitative yield.³⁸



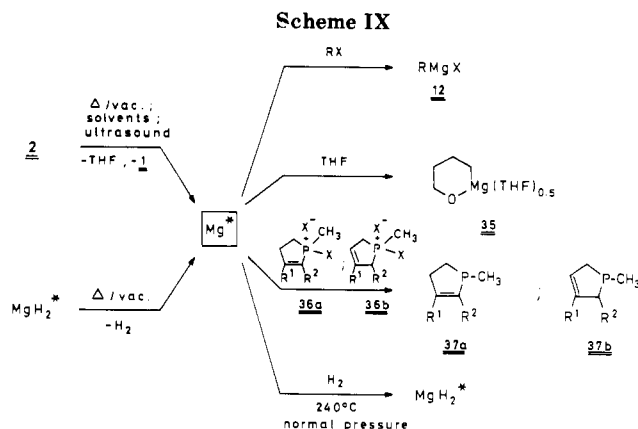
The significance of the catalytic synthesis of magnesium hydride lies primarily in the high chemical reactivity of the latter (see below) relative to ordinary magnesium hydride.³⁹ The extraordinary reactivity of the catalytically prepared magnesium hydride (MgH₂^{*}) is attributed to its generation as extremely fine crystallites (0.05 μm) with a large specific surface area (70–180 m²/g) and an oxide-free surface layer, which is a result of its preparation in an inert-gas atmosphere.

Prior to the discovery of the catalytic synthesis, magnesium hydride found only very limited application in synthesis.³⁹ MgH₂^{*} has opened a vast area of novel possible applications both as an inexpensive raw material for chemical syntheses and as an attractive medium for hydrogen and high-temperature (300–450 °C) heat storage.^{3,36} The following reactions of MgH₂^{*} have been investigated in detail: (i) dehydrogenation/rehydrogenation;^{3,36} (ii) preparation and application of active magnesium (Mg^{*});^{3,16,40} (iii) transformation into orga-

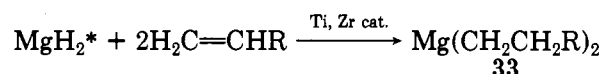
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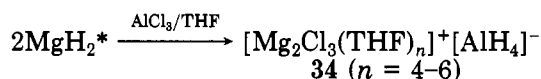
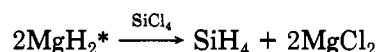


nomagnesium compounds 33 via hydromagnesiumation of 1-alkenes^{5,41–43}



R = H, alkyl, etc.

(iv) synthesis of metal^{44,45} and element hydrides, especially of silane from silicon halides⁴⁶ and of the complex hydride 34 from MgH₂^{*} and AlCl₃ (34 can be used as a substitute for LiAlH₄ in the reduction of numerous organic compounds)⁴⁷



(v) use of MgH₂^{*} as a carrier for heterogeneous catalysts;⁴⁸ and (vi) synthesis of intermetallic compounds and their hydrides and carbides via the reaction of MgH₂^{*} with allylmetal compounds.⁴⁹ All the above-mentioned reactions are difficult or impossible to perform with ordinary magnesium hydride.

The disadvantage of MgH₂^{*} for the purpose of hydrogen and heat storage,³⁶ in spite of its high hydrogen content (7–7.5 wt %) and highly satisfactory H₂ desorption/reabsorption kinetics,³ is its very pyrophoric behavior. For these applications the air-stable Ni-doped magnesium powders, also accessible via magnesium anthracene phase-transfer catalysis, are preferable.³⁶

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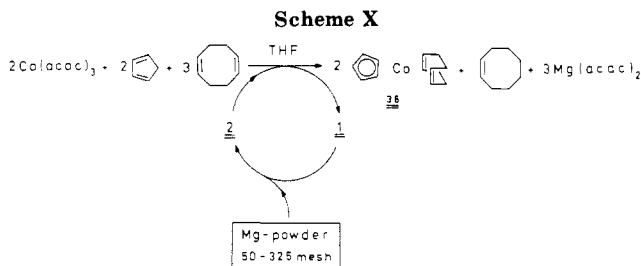
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See ref 50 for potential applications of the active MgH_2/Mg systems for solar heat storage and heat pumps.

Preparation and Application of Active Magnesium (Mg^*) from $MgC_{14}H_{10} \cdot 3THF$ and MgH_2^* . The displacement of the equilibrium between 2 and 1, Mg, and THF (Scheme I) from right to left resulting in the formation of Mg^* can be accomplished either in a solvent or in the solid state.^{6b,8,16} The decomposition of 2 in a solvent, e.g., toluene or ether, at room temperature takes place via $MgC_{14}H_{10} \cdot 2THF$ as intermediate.^{6,8}

The generation of Mg^* from 2 can also be accomplished by heating solid 2 to 200 °C under high vacuum to remove the THF and 1, leaving Mg^* (Scheme IX) as a black highly reactive pyrophoric powder (specific surface area 60–110 m^2/g).^{8,16,40} For the preparation of Mg^* on a larger scale the dehydrogenation of MgH_2^* at >250 °C under vacuum (Scheme IX) or at >300 °C under normal pressure is preferable. The Mg^* prepared by the latter method (specific surface area $\sim 30 m^2/g$) is somewhat less reactive than Mg^* prepared from 2.^{8,16,40}

The Mg^* from either 2 or MgH_2^* has been utilized (Scheme IX) for the generation of Grignard compounds 12,^{8,16,40} the cleavage of THF to give 1-oxa-2-magnesiacyclohexane-0.5THF (35),^{7,16,40,51} and the reduction (e.g., 36a,b to 37a,b) or reductive dimerization of halogenophosphonium halides.⁵² For these types of synthetic applications the reactivity of the Mg^* is comparable to that of Rieke⁵³ or vaporized⁵⁴ magnesium. The Mg^* from 2 or MgH_2^* has also been tested for use as a hydrogen storage material.^{3,8,36,40,55,56} Cf. ref 57 for the reaction of vaporized magnesium⁵⁴ with hydrogen.

Synthesis of Organo-Transition-Metal Complexes. The general synthetic method for organo-

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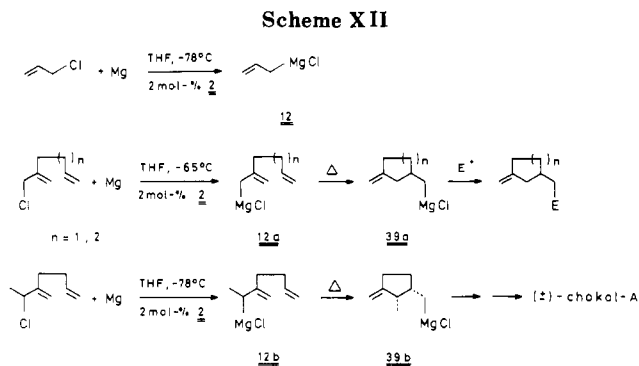
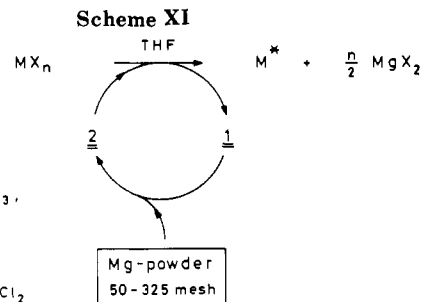
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transition-metal complexes and catalysts involves the reduction of transition-metal salts in the presence of the electron donors.⁵⁸ As compared to other reducing agents, magnesium metal is particularly advantageous in terms of economy, nontoxicity, safety, and availability, but its reactivity is extremely dependent on the size and purity of its active surface.

The observation that the addition of a catalytic amount of 1 to magnesium powder in THF produces 2 as a highly reactive organically solvated form of magnesium in equilibrium with 1 and magnesium metal (Scheme I) established a simple preparative route to a wide range of organo-transition-metal complexes allowing the use of commercial magnesium powder for the reductive synthesis of such compounds.^{32,33}

A typical example is the reduction of $Co(acac)_3$ in the presence of cyclopentadiene, 1,5-cyclooctadiene, and 3–6 mol % of 1 to give $(\eta^5\text{-cyclopentadienyl})(\eta^{2,2}\text{-1,5-cyclooctadiene})cobalt$ (38; Scheme X) in high yield. The synthesis of cobalt complexes has been studied in detail since they are highly effective catalysts for the cyclo-trimerization of alkynes and nitriles to pyridine derivatives.⁵⁹ More recent applications of this route are the syntheses of molybdenum diene complexes,⁶⁰ which are used for the preparation of supported catalysts,⁶¹ and of $Ni(COD)_2$, which is used as a doping agent for the generation of active MgH_2 -Mg hydrogen and high-temperature heat storage systems.^{36,50,55}

Preparation of Finely Divided Metal Powders. Commercial magnesium powder in the presence of catalytic amounts of 1, which produce 2 in THF, has been used as a reducing agent for the preparation of finely divided, highly reactive metal powders (M^*) from metal salts (Scheme XI).²⁹ The specific surface area

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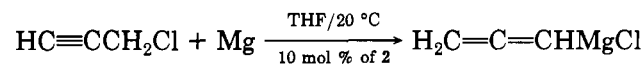
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(6–100 m²/g)²⁹ is comparable to those obtained via alkali-metal reduction^{53,62,63} and metal vapor techniques^{54,63,64} for the generation of active metals.

Generation of Allyl and Allenyl Grignard Compounds. Allylmagnesium chloride (12, Scheme XII) can be generated at -78 °C from magnesium powder and allyl chloride in the presence of 2 mol % of 2.^{8,16,17} The activation of ordinary magnesium powder by catalytic amounts of 2 in THF has also been applied to the synthesis of substituted allyl Grignard reagents 12a³⁴ and 12b³⁵ (Scheme XII) in high yields, which were subsequently cyclized to yield five- or six-membered Grignard reagents 39a and 39b, the latter being a precursor of (±)-chokol-A.³⁵

In the presence of 2, magnesium powder reacts with propargyl chloride in THF to give allenylmagnesium chloride. Since propargyl chloride reacts neither with

ordinary nor with active magnesium (see earlier), it is likely that the reaction takes place via 2 as intermediate.¹⁷



Outlook

The extension of the phase-transfer catalytic reactions discussed here to solvents other than THF and to other metals represents a goal for current research in this field. This would open a way for catalytic synthesis of other inorganic solids, including metals, hydrides, intermetallics, oxides, etc., in a highly reactive or even soluble (e.g., HMgCl) form.

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