Active Metals

- Preparation
- Characterization
- Applications

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Dr. Alois Fürstner
Max-Planck-Institut
für Kohlenforschung
Kaiser-Wilhelm-Platz 1
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Cover illustration: (top) STM image of a 4.1 nm Pd colloid stabilized by $N(nC_8H_{17})_4Br$ (see Chapter 7). M. T. Reetz, W. Helbig, S. A. Quaiser, U. Stimming, N. Breuer, R. Vogel *Science* **1995**, *267*, 367–369. Reproduced with the kind permission of the American Association for the Advancement of Science; (bottom) taxol precursor synthesized by a McMurry coupling using low-valent titanium (see Chapter 3).

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Preface

Many preparative chemists have bad experiences with metal-induced reactions in the early stages of their careers, for example when they try for the first time to start a Grignard reaction. And as the first impression usually persists, many metal-promoted transformations have a bad reputation as being tricky and highly "co-worker dependent".

Indeed, experimental skill is an important prerequisite for many such reactions when they are carried out in a conventional set-up. Since the early recommendations of Grignard himself to use a "crystal of iodine" as initiation agent, many preparative tricks for inducing the reaction have been put forward, evaluated, rejected, and re-introduced. Many other metal-induced transformations share these problems of reproducibility with magnesium chemistry. And even more seriously, only a few metals will (more or less spontaneously) react at all with organic molecules under conventional conditions. However, the various examples described in this book provide clear evidence that this is often not an intrinsic problem of a given metal but rather the consequence of an unsuitable physical form.

The use of activated metals offers convenient solutions to many of the shortcomings mentioned above. This monograph therefore aims to provide a fairly comprehensive overview of those metal activating procedures that are of greatest importance for preparative chemistry and catalysis. In most cases the significant advances achieved result from a substantial alteration of the particle size and texture of the metals employed. All the relevant information on the scope and limitations of the different activation procedures is brought together, and many practical aspects, such as the preparation and handling of the reagents and the specific requirements for chemicals and equipment, are illustrated by the representative laboratory procedures incorporated into the text. This should help the chemist at the bench to find the best solution for a given problem.

Despite these considerable accomplishments, metal activation must remain an immature science until a better insight into the origin of the chemical reactivity becomes possible. The reader will notice that even among different "active" forms of the same metal there may be great differences in the physical properties and chemical performance. We are still far from understanding the intricate phenomenon of activation and the complex processes taking place at a metal–liquid interface. Even the detailed physico-chemical characterization of reactive metal samples using the arsenal of modern solid-state analytical chemistry is only just getting started. Therefore, special emphasis is given in this book to the recent fascinating achievements in this direction. One effect of these has been to teach us important lessons about the discord between generally accepted anticipations and physical reality. For example, some of the activated "metals" have turned out (and others may well do so) not to be zero-valent elements but rather low-valent, polyphasic materials.

We should also keep in mind that finely dispersed (metal) particles deserve some attention as new materials in their own right. Although an in-depth treatment of all these aspects is beyond the scope of this monograph, a lot of information on this rapidly growing area is included. Metal activation is likely to become an important technique not only for preparative organic chemists but also for inorganic chemists and materials scientists. It is beginning to conquer domains that were previously the preserve of metallurgy.

Finally, I should like to take this opportunity to express my sincere gratitude to all the fellow chemists who agreed to write a contribution for this volume. I was lucky to succeed in persuading leading experts to participate in the project. It is their expertise that will familiarize the reader with the essence of the topic.

Mülheim, October 1995 Alois Fürstner

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List of Contributors

L. E. Aleandri
Max-Planck-Institut
für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-45470 Mülheim/Ruhr
Germany

Borislav Bogdanović
Max-Planck-Institut
für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-45470 Mülheim/Ruhr
Germany

Helmut Bönnemann
Max-Planck-Institut
für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-45470 Mülheim/Ruhr
Germany

Werner Brijoux
Max-Planck-Institut
für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-45470 Mülheim/Ruhr
Germany

Jeffrey D. Brown
Department of Chemistry
University of Nebraska-Lincoln
P.O. Box 880304
Lincoln, NE 68588-0304
USA

Galo Cardenas-Trivino
Department of Chemistry
University of Concepcion
Concepcion
Chile

Tian-an Chen
Department of Chemistry
University of Nebraska-Lincoln
P.O. Box 880304
Lincoln, NE 68588-0304
USA

Pedro Cintas
Department of Organic Chemistry
Faculty of Sciences
University of Badajoz
E-06071 Badajoz
Spain

Alois Fürstner
Max-Planck-Institut
für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-45470 Mülheim/Ruhr
Germany

Mark V. Hanson
Department of Chemistry
University of Nebraska-Lincoln
P.O. Box 880304
Lincoln, NE 68588-0304
USA

Wolfgang Helbig
Max-Planck-Institut
für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-45470 Mülheim/Ruhr
Germany

Ferdinand Hofer
Research Institute
for Electron Microscopy
Graz University of Technology
A-8010 Graz
Austria

Kenneth J. Klabunde
Department of Chemistry, Willard Hall
Kansas State University
Mannhattan, KA 66506-3701
USA

Walter R. Klein
Department of Chemistry
University of Nebraska-Lincoln
P.O. Box 880304
Lincoln, NE 68588-0304
USA

Paul Knochel
Fachbereich Chemie
der Universität
D-35032 Marburg
Germany

Thomas Lectka
Department of Chemistry
The Johns Hopkins University
3400 N. Charles Street
Baltimore, MD 21218
USA

Jean-Louis Luche
Université Paul Sabatier
Bâtiment de Chimie
118 Route de Narbonne
F-31062 Toulouse
France

Stefan A. Quaiser
Max-Planck-Institut
für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-45470 Mülheim/Ruhr
Germany

Manfred T. Reetz
Max-Planck-Institut
für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-45470 Mülheim/Ruhr
Germany

Reuben D. Rieke
Department of Chemistry
University of Nebraska-Lincoln
P.O. Box 880304
Lincoln, NE 68588-0304
USA

Matthew S. Sell
Department of Chemistry
University of Nebraska-Lincoln
P.O. Box 880304
Lincoln, NE 68588-0304
USA

Hisashi Yamamoto
Department of Applied Chemistry
Nagoya University
Chikusa
Nagoya 464-01
Japan

Akira Yanagisawa
Department of Applied Chemistry
Nagoya University
Chikusa
Nagoya 464-01
Japan

1 Rieke Metals: Highly Reactive Metal Powders Prepared by Alkali Metal Reduction of Metal Salts

*Reuben D. Rieke, Matthew S. Sell, Walter R. Klein,
Tian-an Chen, Jeffrey D. Brown, and Mark V. Hanson*

1.1 Introduction

In 1972 we reported a general approach for preparing highly reactive metal powders by reducing metal salts in ethereal or hydrocarbon solvents using alkali metals as reducing agents [1]. Several basic approaches are possible and each has its own particular advantages. For some metals, all approaches lead to metal powders of identical reactivity. However, for other metals one method can lead to far superior reactivity. High reactivity, for the most part, refers to oxidative addition reactions. Since our initial report, several other reduction methods have been reported including metal–graphite compounds, a magnesium–anthracene complex, and dissolved alkalides [2].

Although our initial entry into this area of study involved the reduction of $MgCl_2$ with potassium biphenylide, our early work concentrated on reductions without the use of electron carriers. In this approach, reductions are conveniently carried out with an alkali metal and a solvent whose boiling point exceeds the melting point of the alkali metal. The metal salt to be reduced must also be partially soluble in the solvent, and the reductions are carried out under an argon atmosphere. Equation (1.1) shows the reduction of metal salts using potassium as the reducing agent.

$$MX_n + nK \rightarrow M^* + nKX \tag{1.1}$$

The reductions are exothermic and are generally completed within a few hours. In addition to the metal powder, one or more moles of alkali salt are generated. Convenient systems of reducing agents and solvents include potassium and THF, sodium and 1,2-dimethoxyethane (DME), and sodium or potassium with benzene or toluene. For many metal salts, solubility considerations restrict reductions to ethereal solvents. Also, for some metal salts, reductive cleavage of the ethereal solvents requires reductions in hydrocarbon solvents such as benzene or toluene. This is the case for Al, In, and Cr. When reductions are carried out in hydrocarbon solvents, solubility of the metal salts may become a serious problem. In the case of Cr [3], this was solved by using $CrCl_3 \cdot 3\,THF$.

A second general approach is to use an alkali metal in conjunction with an electron carrier such as naphthalene. The electron carrier is normally used in less than stoichiometric proportions, generally 5 to 10% by mole based on the metal salt being reduced. This procedure allows reductions to be carried out at ambient temperature or at least at lower temperatures compared with the previous approach, which requires refluxing. A convenient reducing metal is lithium. Not only is the procedure much safer when lithium is used rather than sodium or potassium, but in many cases the reactivity of the metal powders is greater.

A third approach is to use a stoichiometric amount of preformed lithium naphthalenide. This approach allows for very rapid generation of the metal powders in that the reductions are diffusion controlled. Very low to ambient temperatures can be used for the reduction. In some cases the reductions are slower at low temperatures because of the low solubility of the metal salts. This approach frequently generates the most active metals, as the relatively short reduction times at low temperatures restrict the sintering (or growth) of the metal particles. This approach has been particularly important for preparing active copper. Fujita et al. have shown that lithium naphthalenide in toluene can be prepared by sonicating lithium, naphthalene, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) in toluene [4]. This allows reductions of metal salts in hydrocarbon solvents. This proved to be especially beneficial with cadmium [5]. An extension of this approach is to use the solid dilithium salt of the dianion of naphthalene. Use of this reducing agent in a hydrocarbon solvent is essential in the preparation of highly reactive uranium [6].

For many of the metals generated by one of the above three general methods, the finely divided black metals will settle after standing for a few hours, leaving a clear, and in most cases colorless, solution. This allows the solvent to be removed via a cannula. Thus the metal powder can be washed to remove the electron carrier as well as the alkali salt, especially if it is a lithium salt. Moreover, a different solvent may be added at this point providing versatility in solvent choice for subsequent reactions.

The wide range of reducing agents under a variety of conditions can result in dramatic differences in the reactivity of the metal. For some metals, essentially the same reactivity is found no matter what reducing agent or reduction conditions are used. In addition to the reducing conditions, the anion of the metal salt can have a profound effect on the resulting reactivity. These effects are discussed separately for each metal. However, for the majority of metals lithium is by far the preferred reducing agent. First, it is much safer to carry out reductions with lithium. Second, for many metals (magnesium, zinc, nickel, etc.), the resulting metal powders are much more reactive if they have been generated by lithium reduction.

An important aspect of the highly reactive metal powders is their convenient preparation. The apparatus required is very inexpensive and simple. The reductions are usually carried out in a two-neck flask equipped with a condenser (if necessary), septum, heating mantle (if necessary), magnetic stirrer, and argon atmosphere. A critical aspect of the procedure is that *anhydrous* metal salts must be used. Alternatively, anhydrous salts can sometimes be easily prepared as, for example, $MgBr_2$ from Mg turnings and 1,2-dibromoethane. In some cases, anhydrous salts can be prepared by drying the hydrated salts at high temperatures in vacuum. This approach must be used with caution as many hydrated salts are very difficult to dry completely by this method or lead to mixtures of metal oxides and hydroxides. This is the most common cause when metal powders of low reactivity are obtained. The introduction of the metal salt and reducing agent into the reaction vessel is best done in a dry box or glove bag; however, very nonhygroscopic salts can be weighed out in the air and then introduced into the reaction vessel. Solvents, freshly distilled from suitable drying agents under argon, are then added to the flask with a syringe. While it varies from metal to metal, the reactivity will diminish with time and the metals are best reacted within a few days of preparation.

We have never had a fire or explosion caused by the activated metals; however, extreme caution should be exercised when working with these materials. Until one becomes familiar with the characteristics of the metal powder involved, careful consideration should be taken at every step. To date, no metal powder we have generated will spontaneously ignite if removed from the reaction vessel while wet with solvent. They do, however, react rapidly with oxygen and with moisture in the air. Accordingly, they should be handled under an argon atmosphere. If the metal powders are dried before being exposed to the air, many will begin to smoke and/or ignite. Perhaps the most dangerous step in the preparation of the active metals is the handling of sodium or potassium. This can be avoided for most metals by using lithium as the reducing agent. In rare cases, heat generated during the reduction process can cause the solvent to reflux excessively. For example, reductions of $ZnCl_2$ or $FeCl_3$ in THF with potassium are quite exothermic. This is generally only observed when the metal salts are very soluble and the molten alkali metal approach (method one) is used. Sodium–potassium alloy is very reactive and difficult to use as a reducing agent; it is used only as a last resort in special cases.

1.1.1 Physical Characteristics of Highly Reactive Metal Powders

The reduction generates a finely divided black powder. Particle size analyses indicate a range of sizes varying from 1–2 μm to submicron dimensions depending on the metal and, more importantly, on the method of preparation. In cases such as nickel and copper, black colloidal suspensions are obtained that do not settle and cannot be filtered. In some cases even centrifugation is not successful. It should be pointed out that the particle size analyses as well as surface area studies have been done on samples that have been collected, dried, and sent off for analysis, and are thus likely to have experienced considerable sintering. Scanning electron microscopy (SEM) photographs reveal a range from sponge-like material to polycrystalline material [7]. Results from X-ray powder diffraction studies range from those for metals such as Al and In, which show diffraction lines for both the metal and the alkali salt, to those for Mg and Co, which only show lines for the alkali salt. This result suggests that the metal in this latter case is either amorphous or has a particle size less than 0.1 micrometer. In the case of Co, a sample heated to 300 °C under argon and then reexamined showed diffraction lines due to Co, suggesting the small crystallites had sintered upon heating [8].

ESCA (XPS) and Auger spectroscopy studies have been carried out on several metals and in all cases the metal has been shown to be in the zerovalent state. Bulk analysis also clearly shows that the metal powders are complex materials containing in many cases significant quantities of carbon, hydrogen, oxygen, halogens, and alkali metal.

A BET surface area measurement [9] was carried out on the activated Ni powder showing it to have a specific surface area of $32.7\ m^2\ g^{-1}$. Thus, it is clear that the highly reactive metals have very high surface areas which, when initially prepared, are probably relatively free of oxide coatings. The metals contain many dislocations and imperfections which probably add to their reactivity.

1.2 Rieke Magnesium, Calcium, Strontium, and Barium

The significance of the Grignard reaction is clearly expressed in the following quotation: "... every chemist has carried out the Grignard reaction at least once in his lifetime ..." [10]. In the light of this ubiquity, the generation of new Grignard reagents is indeed a worthwhile endeavor. Although the formation of Grignard reagents is commonly thought to be completely general, there are many organic halides that do not form Grignard reagents. The preparation of Grignard reagents from primary, secondary, and tertiary halides as well as aryl iodides and bromides using ordinary metallic magnesium turnings can be accomplished in a low boiling solvent such as diethyl ether. However, many organic halides including bicyclic bridgehead halides, aryl chlorides, and vinyl chlorides exhibit a low propensity for the formation of their corresponding Grignard reagents via ordinary magnesium turnings. Also, there are many alkyl and aryl bromides which appear to be likely candidates for Grignard formation but fail because of the presence of certain functional groups, such as ethers. Moreover, organic fluorides are generally regarded as inert towards ordinary magnesium. Also, in some cases the Grignard reagents are not stable under the reaction conditions, which commonly involve refluxing in tetrahydrofuran (THF). Clearly, any technique which could make these more difficult organic halides accessible to Grignard reagent formation is desirable. To this end, if ordinary magnesium could be somehow "activated" (either physically or chemically), some of these difficultly accessible Grignard reagents could be prepared. The Rieke method of metal activation has greatly expanded the range of organic halides that are amenable to Grignard reagent preparation.

1.2.1 Formation of Rieke Magnesium

The most common approach for the generation of Rieke magnesium involves a one pot procedure using lithium in conjunction with a catalytic amount of naphthalene (10% by mole based on lithium) in THF under an argon atmosphere. The Rieke magnesium is obtained after vigorous stirring for 3 h. Although the stoichiometric lithium naphthalenide procedure affords Rieke magnesium which is of identical reactivity, the catalytic method is the method of choice because it facilitates work-up.

In an oven-dried, 50-mL, two-necked, round-bottomed flask is placed anhydrous magnesium chloride (0.402 g, 4.22 mmol), lithium (cut foil, 0.061 g, 8.86 mmol) and naphthalene (0.170 g, 1.33 mmol) in a Vacuum Atmospheres Company dry-box under argon. The flask is then connected through an adapter to a double manifold providing vacuum and purified argon, and the flask is evacuated and back-filled with argon three times. Freshly distilled THF (15 mL) from Na/K alloy under argon is added via a syringe. The mixture is stirred vigorously at room temperature for 3 h. The newly formed Rieke magnesium slurry is allowed to settle for 3 h and the supernatant is removed via a cannula. Freshly distilled THF (10 mL) is added to the Rieke magnesium (black powder) followed by the appropriate substrate.

1.2.2 Formation of Rieke Calcium, Strontium, and Barium

The current methodology for the production of Rieke calcium, strontium, and barium is similar to that of magnesium but involves reduction of these metal salts using a stoichiometric amount of lithium biphenylide.

Lithium (9.0 mmol) and biphenyl (9.8 mmol) are stirred in freshly distilled THF (20 mL) under argon until the lithium is completely consumed (ca. 2 h). To a well-suspended anhydrous metal halides (4.4 mmol) in freshly distilled THF (20 mL) solution, the preformed lithium biphenylide is transferred via a cannula at room temperature and stirred for 1 h. The Rieke calcium, strontium, or barium is then ready for use.

1.2.3 Grignard Reactions Using Rieke Metals

The reactions of Rieke magnesium and calcium with various dihaloarenes, some of which react only with difficulty under the conditions of normal Grignard preparations, were recently investigated [11]. It was found that a one-pot, low temperature formation of mono-organometallic intermediates derived from the incorporation of (1 : 1) Rieke magnesium or Rieke calcium with *meta-* and *para-*dihalobenzenes and 2,5-dibromothiophene is possible in very good isolated yields. The ability of Rieke magnesium and calcium to undergo formal oxidative addition reactions with aryl-chlorides, bromides, and fluorides at low temperature is possible owing to the high reactivity of the metal. For example, reaction of 1,4-dibromobenzene and Rieke magnesium (1 : 1) at −78 °C for 30 min formed the mono-organomagnesium intermediate, which when reacted with carbon dioxide followed by acidic hydrolysis, afforded 4-bromobenzoic acid in 99% isolated yield. Similarly, reaction of 1,4-dichlorobenzene and Rieke magnesium (1 : 1) under reflux for 30 min followed by carbon dioxide and acidic hydrolysis afforded 4-chlorobenzoic acid in 95% isolated yield. This is in stark contrast to the reaction of 1,4-dibromobenzene with ordinary magnesium, which affords a mixture of the mono- and di-Grignards, as well as unreacted starting material [12]. Remarkably, reaction of 1,4-difluorobenzene with Rieke calcium (1 : 1) at −78 °C for 30 min, followed by addition of benzaldehyde and acidic hydrolysis afforded 4-fluorobenzhydrol in 93% isolated yield. This one-pot, high yield preparation of mono-organometallic intermediates via Rieke metals could find application in the synthesis of many types of conducting polymers as well as many asymmetrical aryl molecules.

Previous efforts to prepare di-magnesium derivatives of benzene have been successful only with dibromo- or bromoiodobenzene, required forcing conditions, and typically resulted in the mono-magnesium derivative as the major product. This work has been surveyed by Ioffe and Nesmayanov [13]. Using the $MgCl_2$–KI–K–THF system, it was shown that the preparation of the di-Grignard of 1,4-dibromobenzene in 100% yield in 15 min at room temperature is possible. The yield was determined by gas chromatography after hydrolysis and was based on the disappearance of starting material and bromobenzene and the formation of benzene. In earlier work, only one halogen atom of dichloro derivatives of benzene and naphthalene reacted with magnesium [14], and the chlorine atom of *p*-chlorobromobenzene was found to be completely unreactive [15].

We have reported Grignard-type reactions of organocalcium reagents with cyclohexanone [16]. It was found that reactions of aryl halides with Rieke calcium required slightly higher temperatures, up to −30 °C for aryl bromides and up to −20 °C for aryl chlorides. Reactions of *m*-bromotoluene, *m*-bromoanisole, and *p*-chlorotoluene with Rieke calcium gave the corresponding arylcalcium reagents in quantitative yields based on the GC analyses of reaction quenches. As expected, 1,2-addition of these arylcalcium compounds with cyclohexanone gave the alcohols in excellent yields (76%, 79%, and 86%, respectively). Surprisingly, Rieke calcium reacted readily with fluorobenzene at room temperature to form the corresponding organometallic compound which underwent an addition reaction with cyclohexanone to give 1-phenylcyclohexanol in 85% yield. Except for Rieke magnesium prepared by the reduction of magnesium salts [17], few metals undergo oxidative addition with aryl fluorides to form organometallic compounds [18].

A simple example of the advantage of generating Grignard reagents at low temperatures is the reaction of 3-halophenoxypropanes [19]. Although the Grignard reagent is easy to generate at room temperature or above, it eliminates the phenoxy group by an

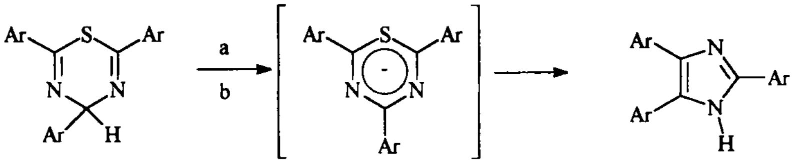
S_N2 reaction, generating cyclopropane. This reaction is, in fact, a standard way to prepare cyclopropanes and the cyclization cannot be stopped; however, by using Rieke magnesium, the Grignard reagent can be prepared at −78 °C and it does not cyclize at these low temperatures. It then can be added to a variety of other substrates in standard Grignard reactions.

When benzonitrile was reacted with Rieke magnesium in refluxing glyme, a deep red color developed after 1 h. Gas chromatography revealed most of the starting material to be unconsumed. After refluxing overnight, the reaction mixture turned brown, and most of the starting material was consumed. An aliquot injected directly into the gas chromatograph did not reveal benzil formation. Work-up showed two main products, 2,4,6-triphenyl-1,3,5-triazine and 2,4,5-triphenylimidazole, in 26% and 27% yields, respectively. These products are shown in Scheme 1-1. The imidazole was quite unexpected but nevertheless present as the most abundant product. A product with a TLC R_f value equivalent to benzil was also present in less than 5 mol % yield, as were numerous other unidentified products in low yields. The imidazole was shown to arise, at least in part, from the triazine. 2,4,6-Triphenyl-1,3,5-triazine reacted with Rieke magnesium in refluxing THF to afford 2,4,5-triphenylimidazole in 27% yield; 65% was unreacted starting material; 8% was unaccounted for.

2,4,6-triphenyl-1,3,5-triazin 2,4,5-triphenylimidazole

Scheme 1-1. Two products formed from reaction of benzonitrile with Rieke magnesium in refluxing glyme.

Giordano and Belli have formed imidazoles from 2,4,6-triaryl-4*H*-1,3,5-thiadiazines via a base-catalyzed extrusion of sulfur [20]. Schmidt et al. also refer to an analogous extrusion of oxygen from the 4*H*-1,3-oxazine [21]. Scheme 1-2 depicts two extrusion reactions used to form imidazoles. Radzisewski has prepared imidazoles by the extrusion of nitrogen from triazines using Zn in refluxing acetic acid [22].



Scheme 1-2. Two extrusion reactions used to form imidazoles. Conditions: (a) aliphatic amines/benzene; (b) *n*-butyllithium.

The trimerization of aromatic nitriles to give symmetrical triazines is not unknown, but generally the reactions must be catalyzed by strong acids or weak bases and carried out under extremely high pressure. The action of *preformed* Grignard reagents also gives symmetrical triazines. Organoalkalis are also known to give trimers but not symmetrical triazines. This direct reaction of magnesium to afford symmetrical triazines is unprecedented in the literature.

1.2.4 1,3-Diene-Magnesium Reagents

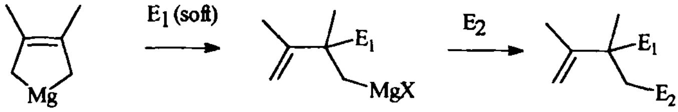
1.2.4.1 Preparation

Metallic magnesium is known to react with certain 1,3-dienes yielding halide-free organomagnesium compounds [23]; however, there is a primary problem associated with the preparation of these reagents. The reaction of ordinary magnesium with 1,3-dienes such as 1,3-butadiene or isoprene is usually accompanied by dimerization, trimerization, and oligomerization. This reaction may be catalyzed by alkyl halides or transition metal salts but is generally accompanied by a variety of by-products and is very time-consuming. Consequently, the utilization of these reagents in organic synthesis has been quite limited [24], except for 1,3-butadiene-magnesium, which has found considerable application in organometallic synthesis [25].

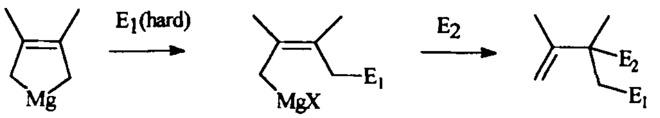
In contrast, Rieke magnesium reacts with (*E,E*)-1,4-diphenyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, isoprene, myrcene, or 2-phenyl-1,3-butadiene in THF at ambient temperature to afford the corresponding substituted (2-butene-1,4-diyl)magnesium complexes in near quantitative yields. The structures of these complexes have not been determined to date except for (1,4-diphenyl-2-butene-1,4-diyl)magnesium, which has been shown to be a five-membered ring metallacycle [26]. Accordingly, the most likely structures for these complexes are five-membered metallacycles or oligomers. It is also possible that an equilibrium exists between these various forms.

1.2.4.2 Regioselectivity

The reactions discussed below illustrate the unusual reactivity of these magnesium-diene complexes. While one might expect the complexes to react as bis-Grignard reagents, it is clear that they are much more powerful nucleophiles. Remarkably, they react with alkyl bromides and chlorides at temperatures as low as −80°C. They appear to react via a standard S_N2 mechanism. However, they can serve as electron transfer agents with certain reagents such as metal salts. With most electrophiles accommodating good leaving groups, clean S_N2 chemistry is observed. Soft electrophiles such as organic halides demonstrate complete regioselectivity for the 2-position as shown in Scheme 1-3. The resulting primary organomagnesium intermediate can then be reacted with a wide range of second electrophiles. Harder electrophiles such as monohalosilanes, monohalostannanes etc. react completely regioselectively in the 1-position as shown in Scheme 1-4. Addition of a second electrophile occurs

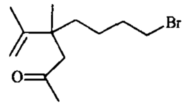
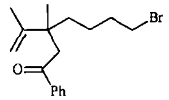
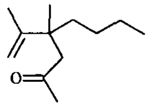
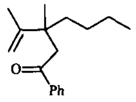
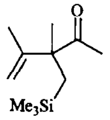
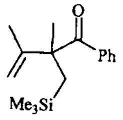
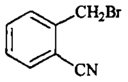
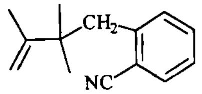
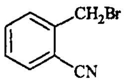
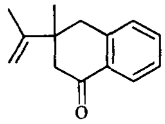
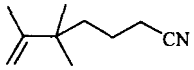


Scheme 1-3. Reaction of a soft electrophile with (2,3-dimethyl-2-butene-1,4-diyl)magnesium.



Scheme 1-4. Reaction of a hard electrophile with (2,3-dimethyl-2-butene-1,4-diyl)magnesium.

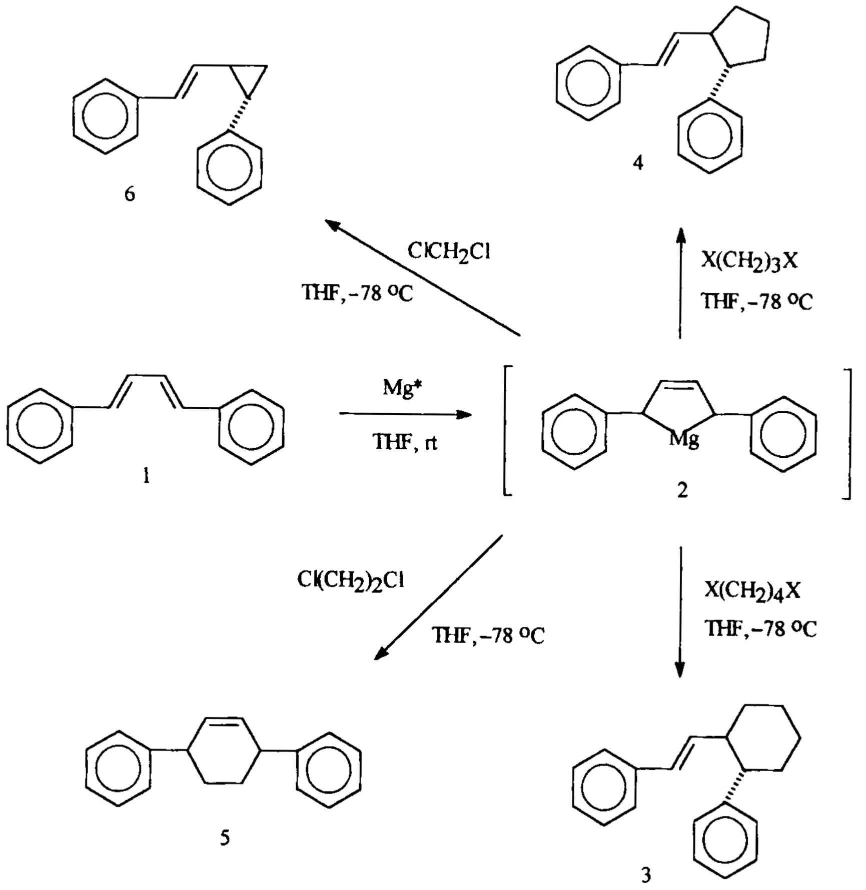
Table 1-1. Stepwise reactions of (2,3-Dimethyl-2-butene-1,4-diyl)magnesium.

Entry	E_1	E_2	Product	Yield (%)
1	$Br(CH_2)_4Br$	MeCOCl		62
2	$Br(CH_2)_4Br$	PhCOCl		60
3	$Me(CH_2)_3Br$	MeCOCl		61
4	$Me(CH_2)_3Br$	PhCOCl		82
5	Me_3SiCl	MeCOCl		73
6	Me_3SiCl	PhCOCl		79
7		H_3O^+		35
8		-		30
9	$Br(CH_2)_3CN$	H_3O^+		58

primarily in the 2-position. The overall result is that one can effect a net 2,1-addition or a 1,2-addition by choosing appropriate electrophiles. Complex, highly functionalized molecules have been prepared using this approach and are shown in Table 1-1 [27].

1.2.4.3 Carbocyclization of (1,4-Diphenyl-2-butene-1,4-diyl)magnesium with Organic Dihalides

(*E*,*E*)-1,4-Diphenyl-1,3-butadiene has been found to be one of the most reactive conjugated dienes towards metallic magnesium. Reaction of this diene with Rieke magnesium affords (1,4-diphenyl-2-butene-1,4-diyl)magnesium (**2**) which can be treated with various electrophiles (Table 1-2). Reactions of **2** with 1,*n*-dibromoalkanes resulted in either cyclization or reduction of the electrophile, depending on the initial dibromide. For example, cyclization proceeded rapidly at –78 °C in the reaction of **2** with 1,3-dibromopropane or 1,3-dichloropropane, yielding a single product, *trans*-1-phenyl-2-((*E*)-2-phenylethenyl)cyclopentane (**4**) in 65% or 81% isolated yield, respectively (Scheme 1-5). Similar cyclizations were obtained with (2,3-dimethyl-2-buten-1,4-diyl)-magnesium (Table 1-3).

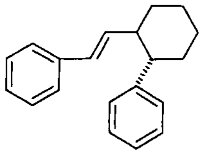
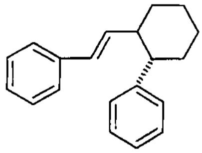
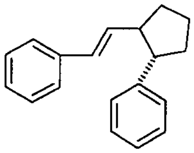
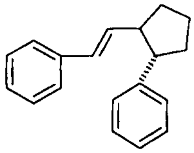
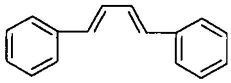
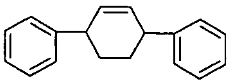
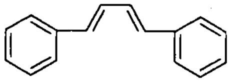
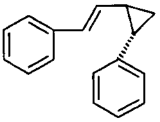
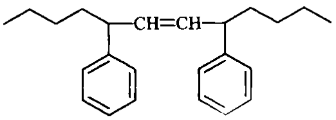
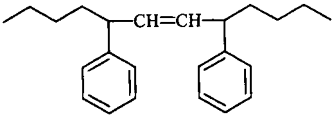
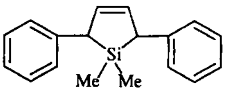


Scheme 1-5. Carbocyclization of (1,4-diphenyl-2-butene-1,4-diyl)magnesium with organic dihalides [27].

(1,4-Diphenyl-2-butene-1,4-diyl)magnesium can be easily prepared using Rieke magnesium. Treatment of the diene-magnesium reagent with 1,*n*-dihaloalkanes provides a convenient method for the generation of substituted three-, five-, and six-membered carbocycles. Significantly, the cyclizations are always stereoselective and completely regioselective.

It should be noted that the (1,4-diphenyl-2-butene-1,4-diyl)barium complex has recently been prepared in our laboratories [28] and exhibits higher reactivity than its magnesium-diene counterpart.

Table 1-2. Reaction of (1,4-diphenyl-2-butene-1,4-diyl)magnesium with electrophiles.

Entry	Electrophile	Product	Yield (%)
1	$Br(CH_2)_4Br$		40
2	$Cl(CH_2)_4Cl$		51
3	$Br(CH_2)_3Br$		65
4	$Cl(CH_2)_3Cl$		81
5	$Br(CH_2)_2Br$		–
6	$Cl(CH_2)_2Cl$		59
7	$BrCH_2Br$		–
8	$ClCH_2Cl$		76
9	$CH_3(CH_2)_3Br$	 (cis/trans = 56:44)	93
10	$CH_3(CH_2)_3Cl$	 (cis/trans = 28:72)	87
11	Me_2SiCl_2		66