CHEMICAL SYNTHESIS USING HIGHLY REACTIVE METALS

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Preface

It is obvious that such a large body of work as the summary of our active metal research for over 50 years requires the acknowledgement of many people. There is also no doubt that there is one key person without whose lifelong help this book would not be possible. That person is my wife Loretta. From the day we met at the entrance examinations for the chemistry graduate program at the University of Wisconsin–Madison in September 1961 until today, she has been of incredible help. From our early days at the University of North Carolina at Chapel Hill, where she carried out research with my research group, to 1991 when the two of us founded Rieke Metals, Inc., in Lincoln, Nebraska, where she served as Vice President and Business Manager, she has been a cornerstone of my travels through life. Another major force in these efforts is our daughter Elizabeth, who started working part time in Rieke Metals, Inc., and rose to the position of CEO before we sold the company in July 2014. Finally, our son Dennis was a constant supporter of our efforts and an excellent sounding board for our ideas.

Of course, this work would not be possible if I did not have an excellent group of graduate students, postdoctoral students, and undergraduate students. From the initial two students who worked on the active metals, Dr. Phillip Hudnall and Dr. Steven Bales, to my final student, Dr. S. H. Kim, I had an outstanding group of people to work with. This book only covers my research on active metals so my students that worked on radical anion chemistry, electrochemistry, electron paramagnetic chemistry, and quantum mechanical calculations are not mentioned in the book. The active metal students are all referenced in this book in the metal sections that they were involved with. Of special note is my postdoctoral student from Spain, Professor Alberto Guijarro of the University of Alicante, Alicante, Spain, who carried out the beautiful mechanistic studies on the oxidative addition of Rieke zinc with organic halides as well as several synthetic studies. The three years he spent with us were particularly productive. The history of active metals is discussed in the early part of the book. However, special thanks must go to Professor Saul Winstein of UCLA who allowed me to follow my idea of studying through-space interactions by preparing radical anions and determining their EPR spectra. My other mentors, my undergraduate research director at the University of Minnesota–Minneapolis, Professor Wayland E. Noland, and my PhD mentor, Professor Howard E. Zimmerman of the University of Wisconsin–Madison, were also of major help in my early training.

Of final note is the assistance of our cat, Buddy. He always felt that it was his duty to come and sit in the middle of my papers as I was writing this book. When he was banished to the side of the papers, he insisted on placing his head and two front paws on my arm.

Chemical research is a long, hard road but the rewards of discovery are hard to describe. As the old saying goes, the train ride has been long and many times bumpy, but we have not reached the station yet.

1

Genesis of Highly Reactive Metals

Modern life without metals is inconceivable. We find them at every turn in our existence: transportation, buildings and homes, transporting our water, carrying our electricity, modern electronics, cooking utensils, and drinking vessels. Perhaps this is not to be unexpected as 91 of the 118 elements in the periodic table are metals. Accordingly, we can surely expect to find them in all aspects of our lives. The early chemistry of metals or processing of metals is one of the oldest sciences of mankind. Its history can be traced back to 6000 BC. Gold was probably the first metal used by man as it can be found as a relatively pure metal in nature. It is bright and attractive and is easily formed into a variety of objects but has little strength and accordingly was used mainly for jewelry, coins, and adornment of statues and palaces. Copper articles can also be traced to ~6000 BC. The world's oldest crown made of copper was discovered in a remote cave near the Dead Sea in 1961 and dates to around 6000 BC. The smelting of copper ores is more difficult and requires more sophisticated techniques and probably involved a clay firing furnace which could reach temperatures of 1100–1200°C. Silver (~4000 BC), lead (~3500 BC), tin (~1750 BC), smelted iron (~1500 BC), and mercury (~750 BC) constituted the metals known to man in the ancient world. It would not be until the thirteenth century that arsenic would be discovered. The 1700s, 1800s, and 1900s would see the rapid discovery of over 60 new metals. The bulk of these metals were prepared by reducing the corresponding metal salt with some form of carbon or, in a few cases, with hydrogen. A small number of difficult to free metals were eventually prepared by electrochemical methods such as the metals sodium, potassium, and aluminum. Eventually the concept of a metal alloy was understood. It became readily apparent that the presence of one or more different metals dispersed throughout a metal could dramatically change the chemical and physical properties of any metal. The extensive and broad field of metal alloys will not be discussed in this text. The main point to be made is that the presence of a foreign material, whether it be another metal or a nonmetal, can have a significant effect on a metal's chemical and physical properties. Pure metals prepared by different methods have essentially all the same chemical and

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physical properties. The one caveat in this statement is particle size or surface area. Whitesides clearly demonstrated the effect of surface area on the rate of Grignard formation at a magnesium surface. Taking this to the extreme, Skell and Klabunde have demonstrated the high chemical reactivity of free metal atoms produced by metal vaporization. These two topics will be discussed in greater depth later in the text. Thus it is clear that preparation of metals which leads to the presence of foreign atoms throughout the metal lattice can have a profound effect on the metal's chemical and physical properties. This will be discussed in greater detail later in the text.

The genesis of highly reactive metals from our laboratories can be traced back to my time spent in a small two-room schoolhouse in a small town of 180 people in southern Minnesota (1947–1949) and then to graduate school at the University of Wisconsin–Madison where I was working on my PhD degree under the direction of Professor Howard E. Zimmerman. My research proposal, which was part of the degree requirements, was the synthesis of the naphthalene-like molecule shown in Figure 1.1. The ultimate goal of the project was to determine if there was through-space interaction between the two 1,3-butadiene units via the bridging ethylene unit (4N + 2 electrons). To verify the through-space interaction, I proposed preparing the radical anion and measuring the electron paramagnetic resonance (EPR) spectrum. EPR became an available experimental technique, thanks to the explosion of solid-state electronics in the 1960s. Simulating the spectrum in conjunction with quantum mechanical calculations should provide a reasonable estimate of the influence of through-space interaction. My postdoctoral mentor, Professor Saul Winstein, at UCLA allowed me to pursue this general idea and we went on to produce the monohomocyclooctatetraene radical anion. The experience gained in this project working with solvated electrons in THF allowed me to write my first proposal as an assistant professor of chemistry at the University of North Carolina at Chapel Hill. The project was the reduction of 1,2-dibromobenzocyclobutene with solvated electrons to generate the radical anion of benzocyclobutadiene as shown in Figure 1.2. The reduction was to be carried out in the mixing chamber of a flow mixing reactor in the sensing region of an EPR spectrometer. However, even at −78°C, the only spectrum we could see was the radical anion of benzocyclobutene. It became clear that the radical anion (II) and/or the dianion was so basic that even at −78°C in extremely dry THF, the anions were protonated to yield benzocyclobutene which was then reduced to the radical anion. Quenching with D_2O verified the presence of **II** and its dianion. In order to trap or stabilize the dianion, we attempted to carry out this chemistry in the presence of $MgCl_2$ and generate the di-Grignard. However, we mistakenly mixed the solvated electrons (we were using potassium naphthalenide) with $MgCl_2$, generating a black slurry of finely divided black

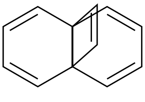

Figure 1.1 Graduate research proposal.

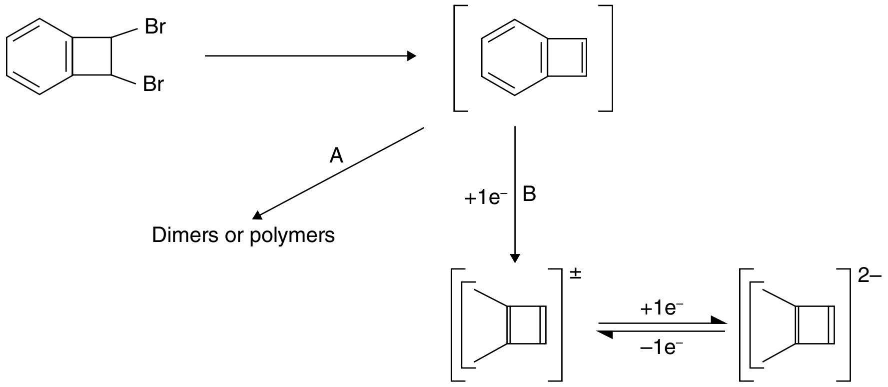

Figure 1.2 First research proposal.

metal. Upon reflection, it became clear that we had generated finely divided magnesium. We quickly determined that this magnesium was extremely reactive with aryl halides and generated the corresponding Grignard reagent. Thus, the field of generating highly reactive metals by reduction of the metal salts in ethereal or hydrocarbon solvents was born.

2

General Methods of Preparation and Properties

2.1 General Methods for Preparation of Highly Reactive Metals

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 [1–5]. 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 [6].

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 2.1 shows the reduction of metal salts using potassium as the reducing agent:

$$MX_n + nK \rightarrow M^* + nKX \tag{2.1}$$

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

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are carried out in hydrocarbon solvents, solubility of the metal salts may become a serious problem. In the case of Cr [7], 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 5–10% 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 also 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 use 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 [8]. This allows reductions of metal salts in hydrocarbon solvents. This proved to be especially beneficial with cadmium [9]. 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 [10].

For many of the metals generated by one of the three general methods in the preceding text, 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.

Finally, a fourth approach using lithium and an electron carrier such as naphthalene along with $Zn(CN)_2$ yields the most reactive zinc metal of all four approaches [11].

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-necked 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. With the exception of some forms of magnesium, 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, especially magnesium. 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.

2.2 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 to 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 analysis and 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 spongelike material to polycrystalline material (Figures 2.1 and 2.2). 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 <0.1 μm. In the case of Co, a sample heated to 300°C under argon and then reexamined showed diffraction lines due to Co, suggesting that the small crystallites had sintered upon heating [12].

ESCA (XPS) 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

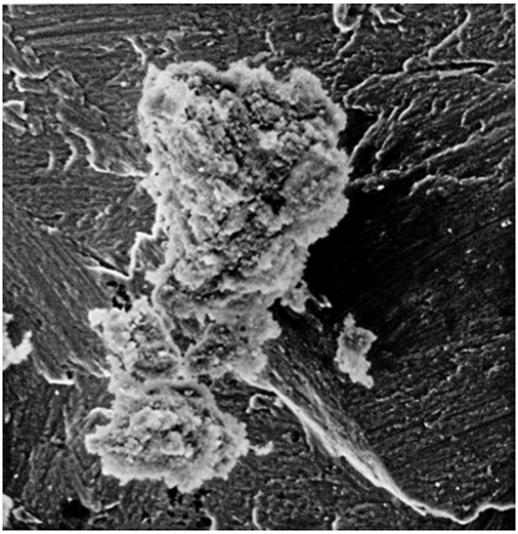

Figure 2.1 Active magnesium.

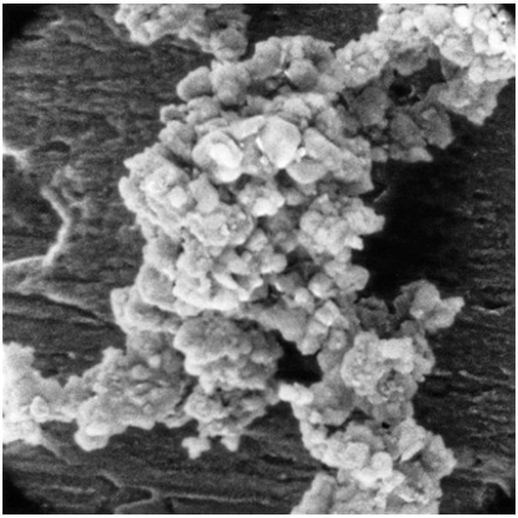

Figure 2.2 Active indium.

significant quantities of carbon, hydrogen, oxygen, halogens, and alkali metal. A BET [13] surface area measurement was carried out on the activated Ni powder showing it to have a specific surface area of 32.7 m^2/g. 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.

2.3 Origin of the Metals' High Reactivity

There are several characteristics of the metal powders prepared by these methods which clearly explain their high reactivity. They all exhibit very high surface areas. Particle sizes of a few microns or in some cases <0.1 μm point to very high surface areas. The BET studies [13] on Ni powder indicated surface areas of over 30 m^2/g. Moreover, the lack of diffraction lines for several metals suggests particle sizes of <0.1 μm. Also the possibility of some metals being amorphous would increase their internal energy and lead to higher reactivity compared to the corresponding highly crystalline counterpart. In addition, the metals are produced under nonequilibrium conditions and exhibit many dislocations and imperfections. This would also be expected to lead to increased chemical reactivity. The metals are also prepared under a pure argon atmosphere which would result in a relatively oxide-free surface being produced. Bulk analysis of the metals is quite varied depending on the metal. However, in all cases, there is a significant amount of other elements generally including carbon, hydrogen, halogens, and alkali metal ions from the alkali metal reducing agent. As will be pointed out in detail later, finely divided metal powders prepared by methods which do not introduce these materials into the metal lattice are all significantly less reactive than Rieke metals. For example, metal powders prepared by metal vaporization methods are far less reactive in oxidative addition reactions compared to the corresponding Rieke metals even though they are of comparable or even smaller particle size [14]. There is also one extremely important difference between the Rieke metals and finely divided metals prepared by other methods, and that is the presence of alkali metal salts. Whitesides' [15] work on magnesium and our studies [16] on zinc clearly show that the rate-determining step in oxidative addition reactions is the electron transfer from the metal surface to the organic halide. As in an electrochemical reduction reaction, the alkali salt can act as an electrolyte and facilitate this electron transfer. In most of the reductions presented in this text, the alkali salt is LiCl or LiBr. We will see later in the text that these alkali salts can also increase the reactivity of the resulting organometallic reagents RMX toward many electrophiles. In summary, the Rieke method of producing metal powders yields metals which are far from pure metal powders. The presence of these foreign materials along with the features mentioned yields metal powders which undergo many new and novel reactions which cannot be achieved by standard metals or their chemically activated counterparts.

References

1 Rieke, R.D.; Hudnall, P.M. *J. Am. Chem. Soc.* 1972, **94**, 7178.

2 Rieke, R.D.; Hudnall, P.M.; Uhm, S. *J. Chem. Soc. Chem. Commun.* 1973, 269.

3 Rieke, R.D.; Bales, S.E. *J. Chem. Soc. Chem. Commun.* 1973, 739.

4 Rieke, R.D.; Bales, S.E. *J. Am. Chem. Soc.* 1974, **96**, 1775.

5 Rieke, R.D.; Chao, L. *Synth. React. Inorg. Met.-Org. Chem.* 1974, **4**, 101.

6 (a) Csuk, R.; Glanzer, B.L.; Furstner, A. *Adv. Organomet. Chem.* 1988, **28**, 85. (b) Savoia, D., Trombini, C., Uamni-Ronchi, A. *Pure Appl. Chem.* 1995, **57**, 1887. (c) Bogdanovic, B. *Acc. Chem. Res.* 1988, **21**, 261. (d) Marceau, P., Gautreau, L., Beguin, F. *J. Organomet. Chem.* 1991, **403**, 21. (e) Tsai, K.L.; Dye, J.L. *Am. Chem. Soc.* 1991, **113**, 1650.

7 Rieke, R.D.; Ofele, K.; Fischer, E.O. *J. Organomet. Chem.* 1974, **76**, C19.

8 Fujita, T.; Watanaba, S.; Suga, K.; Sugahara, K.; Tsuchimoto, K. *Chem. Inad. (London).* 1983, **4**, 167.

9 Burkhardt, E.; Rieke, R.D. *J. Org. Chem.* 1985, **50**, 416.

10 (a) Kahn, B.E.; Rieke, R.D. *Organometallics* 1988, **7**, 463. (b) Kahn, B.E.; Rieke, R.D. *J. Organomet. Chem.* 1988, **346**, C45.

11 Hanson, M.; Rieke, R.D. *Synth. Commum.* 1995, **25**, 101.

12 Rochfort, G.L.; Rieke, R.D. *Inorg. Chem.* 1986, **25**, 348.