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

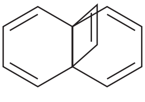

Figure 1.1 Graduate research proposal.

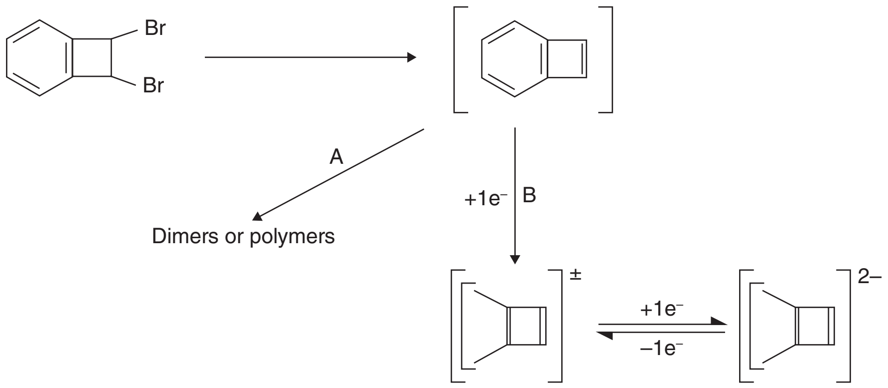

Figure 1.2 First research proposal.

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.