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SIMPLE AND COMPLEX METAL HYDRIDES OF THE MAIN GROUP METALS. A PERSONAL ACCOUNT OF THE EARLY DAYS

E.C. ASHBY

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332 (U.S.A.)

I feel, like many others writing an article to commemorate Volume 200 of the *Journal of Organometallic Chemistry*, i.e. it is an unusual opportunity to reminisce about the early days of a major interest in one's research career. It would be interesting to review the early days of a number of our research interests, however, I have chosen the area of main group metal hydride chemistry. This area was probably the most confused, in the early days when we first became involved, of any of the areas in which we have worked.

When I was a graduate student at the University of Notre Dame (1954–1956), I first became acquainted with main group metal hydride chemistry and main group organometallic Chemistry. My Ph.D. work was in the area of organoboron chemistry and one of my favorite teachers was Professor Ernest Eliel who was doing work with LiAlH_4 and mixed hydride reagents. I found both organometallic and metal hydride chemistry very fascinating because of the unique synthetic possibilities that these classes of compounds afforded and because of the unusual experimental skill needed in working with such compounds.

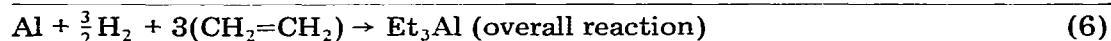
The relationship between metal alkyls and metal hydrides is, of course, quite close in that each can be easily converted to the other, i.e. a main group metal alkyl eliminates olefin to form a metal hydride on heating and in many cases the metal hydride will add back to the olefin at room temperature to form the corresponding metal alkyl. A well known case involves the olefin elimination observed on heating tri-*n*-butylborane [1] (eq. 1) and the well known readdition (hydroboration) of the resulting boron hydride to the olefin [2] (eq. 2). It was during my graduate student days that we first observed that trialkyl-



boranes such as $n\text{-Bu}_3\text{B}$ gave on distillation $n\text{-Bu}_2\text{BH}$ and a mixture of 1- and 2-butenes [1] followed soon thereafter by Professor H.C. Brown's discovery that boranes add readily to olefins in THF solvent (hydroboration) [2].

My dedicated interest in metal hydride chemistry began however in 1956, soon

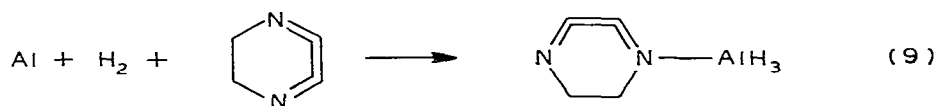
after I joined the Ethyl Corporation in Baton Rouge, Louisiana, when I was exposed to the work of Professor Karl Ziegler. Ziegler and co-workers found that they could prepare Et_3Al from aluminum, hydrogen, and ethylene (eq. 6) and suggested the following series of reactions (eqs. 3–5) to explain their results [3].



To be able to prepare Et_3Al from aluminum, hydrogen and ethylene was indeed a fantastic accomplishment, but what caught my attention was the suggestion by Ziegler that AlH_3 was an intermediate in the main reaction; formed by the reaction of aluminum and hydrogen. Aluminum hydride was a known compound and it was also known to be soluble in THF. Because of the previous work of Eliel [4] and W.G. Brown [5], I thought that AlH_3 would make an excellent reducing agent for organic functional compounds, especially since it was soluble in THF and especially if it could be formed so economically from aluminum metal and hydrogen. I carried out a few experiments attempting to react activated aluminum powder with hydrogen in various solvents, however I could never detect a trace of AlH_3 . I was then able to show that AlH_3 decomposes rapidly at those temperatures ($90\text{--}120^\circ\text{C}$) at which aluminum metal and hydrogen react at an appreciable rate, therefore if AlH_3 was being formed in the reaction, it is clear that it was decomposing as fast as it was being formed. I then decided to trap the AlH_3 , if it was indeed formed in situ, by adding some trapping agent that would form a more stable product than AlH_3 itself and preferably one more stable at temperatures $>140^\circ\text{C}$. A quick search of the literature showed that AlH_3 reacts with both trimethylamine [6] and sodium hydride [7]. The reported reactions are shown in eqs. 7 and 8.



The reaction of aluminum, hydrogen, and trimethylamine did not produce $(\text{CH}_3)_3\text{N}-\text{AlH}_3$ because, as we soon found out, the amine-alane was no more stable than AlH_3 itself. Once again, the temperature necessary for aluminum and hydrogen to react at an appreciable rate (140°C) exceeded the decomposition temperature of the amine-alane product. However, the use of triethylene-diamine (DABCO) did result in the formation of an amine-alane (eq. 9) in quantitative yield since the product was stable to over 200°C [8].



Encouraged by this result, I added NaH to aluminum and hydrogen (eq. 10)

and much to my delight, NaAlH_4 was formed in quantitative yield in the first experiment [9]. Since it is very reasonable to presume that NaH could easily be formed in situ by the reaction of sodium and hydrogen, we found that the



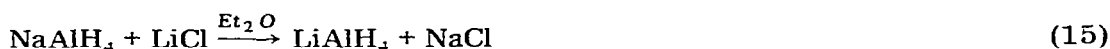
reaction could be carried out using sodium instead of sodium hydride (eq. 11) [10].



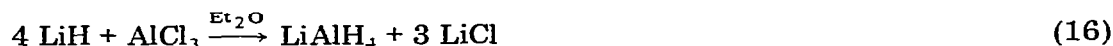
This reaction works equally as well with lithium, potassium or cesium hydride, to form the corresponding aluminohydride (MAlH_4) in nearly quantitative yield and in a high state of purity (eq. 12–14) [10].



During these studies a colleague, Dr. Gene Robinson, showed that LiAlH_4 could also be readily prepared by the reaction of NaAlH_4 and LiCl in diethyl ether [10,11].



One of the important aspects of the discovery of the preparation of NaAlH_4 from the elements is the economics of such a process. We had shown that NaAlH_4 reduces organic functional compounds in the same way and at approximately the same rate as LiAlH_4 . Since LiAlH_4 is prepared from lithium hydride and AlCl_3 [12] (eq. 16) and the hydrogen used to form LiAlH_4 all comes from LiH (Li metal \sim \$16/lb) [13], it is clear that LiAlH_4 prepared by this method



will be expensive (\sim \$40/lb) [14] and hence have limited applications. However, the hydrogen used to form NaAlH_4 by the direct process, comes from hydrogen gas and the carrier, sodium, is much less expensive (\$0.30/lb) than lithium. Indeed the Ethyl Corporation under the direction of Dr. Gottfried Brendel made 100 lb quantities of NaAlH_4 by the direct synthesis process (eq. 17) in a 100 gal autoclave. The cost of NaAlH_4 prepared by this process should be in the



\$2–5/lb range and thus could become more available for a multitude of applications.

The interesting chemistry that could be carried out with the $\text{Al}-\text{H}_2$ system

was not over with the direct synthesis of NaAlH_4 . A former colleague and good friend at the Ethyl Corporation, Paul Kobetz (now deceased) and I were able to show that an interesting new class of hydrides, the hexahydrides could also be prepared from the elements [15]. We prepared Na_3AlH_6 (eq. 18) in much the same way as NaAlH_4 except for a change in reaction stoichiometry. Later on while at Georgia Tech, Dr. Bruce James, a postdoctoral assistant, prepared K_3AlH_6 by a similar process (eq. 19) [16].



Both Na_3AlH_6 and K_3AlH_6 proved to be compounds of unusual thermal stability (dec. $>200^\circ\text{C}$), insolubility in organic solvents and effective reducing power toward organic functional compounds.

After seven years with the Ethyl Corporation (1956–1963) I managed to obtain a position as Assistant Professor with Georgia Tech, mostly through the help of H.C. Brown, Ernest Eliel and Dietmar Seyferth, three chemists who helped me in many ways to get started in academia. When I arrived at Georgia Tech in 1963 there was little with which one could begin research, however with the full support of the Chairman, Dr. Monroe Spicer, I began to put together a research laboratory and most importantly a high pressure laboratory with which we could continue the Al-H_2 work. Soon thereafter appeared, much to my good fortune, a remarkable young man, Dr. Roger Kovar, fresh from his Ph.D. with George Morgan at the University of Wyoming. I suggested to Dr. Kovar that if AlH_3 is indeed an intermediate in the reaction of aluminum metal with hydrogen, we should be able to react aluminum and hydrogen with secondary and primary amines to form the corresponding amino and iminoalanes. Dr. Kovar, one of the finest experimentalists with whom I have been associated, quickly and precisely carried out experiments which showed that such preparations were possible (eqs. 20–21).

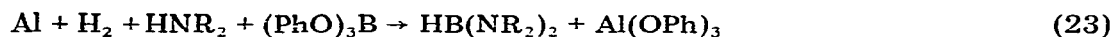


The bis-dialkylaminoalanes were formed in quantitative yield and subsequently shown to be very soluble in hydrocarbon solvents [17]. These compounds are not only excellent reducing agents toward organic functional compounds, but we have recently found them to be excellent hydroaluminating agents (eq. 22) [18]. Since the $\text{HAl}(\text{NR}_2)_2$ compounds are prepared so economically and the reaction is rapid and nearly quantitative, such a reaction holds great promise in

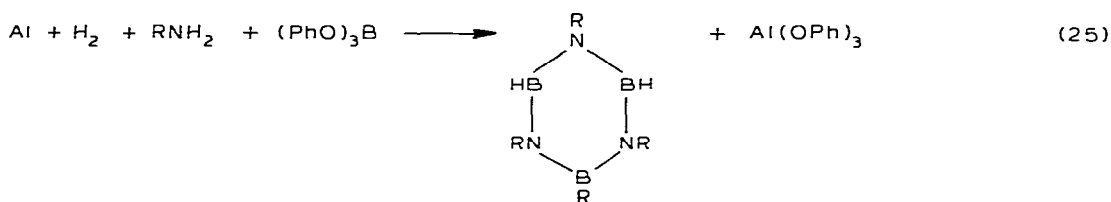
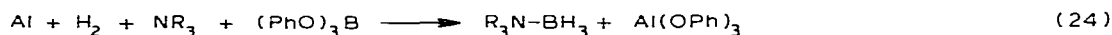


synthetic organic chemistry. We were able to prepare iminoalanes in high yield which have been shown by others to be excellent polymerization catalysts [19]. We further reasoned that if $\text{HAl}(\text{NR}_2)_2$ compounds can be formed from aluminum, hydrogen and secondary amines, it should be possible to add a borate

ester to the reaction mixture and form the corresponding $\text{HB}(\text{NR}_2)_2$ compounds. Indeed this reaction proceeds very well to form bis-dialkylaminoboranes in high yield [20]. These compounds likewise are hydrocarbon soluble and excellent reducing agents.



Possibly even more interesting was the substitution of tertiary and primary amines in the above reaction. Tertiary amines were found to form the tertiary amine boranes in high yield and the primary amines were found to form the corresponding borazines (borazoles) [22]. The above methods are indeed the easiest and most economical methods for the preparation of amine boranes, aminoboranes and borazines.



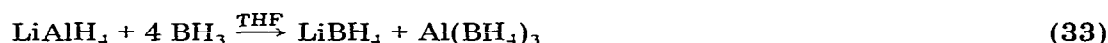
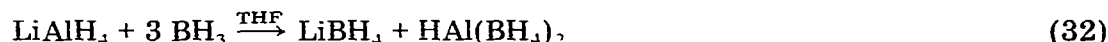
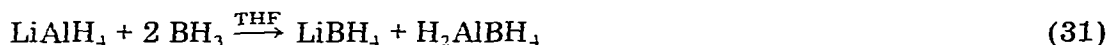
At this point our interest in main group metal chemistry was high. We were having success and a lot of fun developing economical methods for the preparation of compounds that have been available only in minute quantities at considerable expense. However, at this stage as an organic chemist, I was interested in preparing new metal hydrides for use as stereoselective reducing agents in organic synthesis. I felt that LiAlH_4 and NaBH_4 were two of the most important reagents in synthetic organic chemistry and yet no one had attempted to prepare new complex metal hydrides e.g. where the central metal is a Group IIA rather than Group IIIA metal. My plan was first to prepare some known complex metal hydrides and test their stereoselectivity before proceeding to make more new hydrides. There were three classes of hydrides already reported in the literature that interested me, so my students and I set out to prepare these compounds for testing. These compounds were (1) the $\text{LiAlH}_n(\text{BH}_4)_{4-n}$ compounds [23], (2) the Group IIA complex aluminohydrides, $\text{Mg}(\text{AlH}_4)_2$ [24] and $\text{Be}(\text{AlH}_4)_2$ [25] and (3) the HMgX compounds (where $\text{X} = \text{Cl}, \text{Br}$ and I) [26]. To summarize our results at this point, I can simply say that all of the reports describing these compounds were in error and indeed none of these compounds had been prepared by the described methods. Since many of these compounds are rather fundamental and represented a significant portion of the known metal hydride chemistry at that time, such findings about these reports caused me to think carefully about most reports in this area.

The report concerning $\text{LiAlH}_n(\text{BH}_4)_{4-n}$ compounds [23] was most interesting (eqs. 26–29) in that two of these compounds [$\text{LiAlH}_3\text{BH}_4$ and $\text{LiAlH}_2(\text{BH}_4)_2$] were reported to be unusually thermally stable. One can calculate a rather high specific impulse (Isp) for these hydrides in combination with a N—F

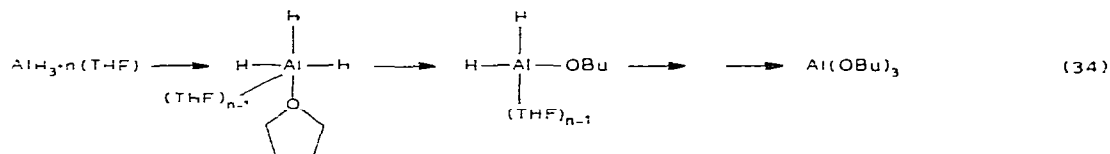
oxidizer and hence we had an interest in these compounds not only as reducing



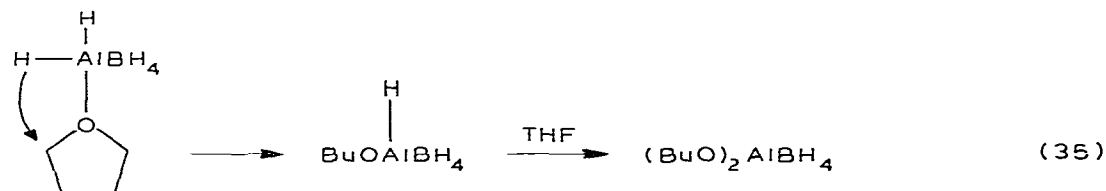
agents, but also as solid rocket propellants. It turned out however, that the above reactions do not take place as represented in eqs. 26–29, but rather other products are formed instead; quantitatively (eqs. 30–33) [27].



The two products from each reaction were easily separated by simply removing the THF solvent at room temperature under vacuum, followed by the addition of benzene. The LiBH_4 precipitated as a white crystalline solid and the THF adducts of the $\text{AlH}_n(\text{BH}_4)_{3-n}$ compounds were soluble in benzene. They were easily identified by infrared spectroscopy and elemental analysis. The previous workers did not separate products, but simply isolated the total reaction product and analyzed for aluminum and boron. The thermal stability (300°C) of the product reported to be $\text{LiAlH}_3\text{BH}_4$ can be explained when it is realized that the product stable to 300°C is actually $\text{Al}(\text{OBU})_3$ formed by THF cleavage of AlH_3 (eq. 34). Since the reported product was heated to test the thermal stability, it



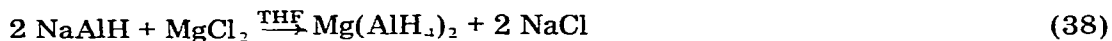
is not surprising that THF cleavage takes place during the heating process. Actually we also showed that H_2AlBH_4 , if isolated within 15 min of reaction, shows an Al–H stretching band at 5.6μ in the infrared region; however, if the compound remains in solution 24 hours before work up, the Al–H stretching band disappears and $(\text{BuO})_2\text{Al}-\text{BH}_4$ is isolated (eq. 35). Interestingly $(\text{BuO})_2\text{AlBH}_4$ decomposes at 200°C , the same temperature of decomposition reported for $\text{LiAlH}_2(\text{BH}_4)_2$. Needless to say, we could find no evidence for stable $\text{LiAlH}_n(\text{BH}_4)_{4-n}$ compounds.



The next surprising result involved $\text{Mg}(\text{AlH}_2)_2$. Its preparation was reported from LiAlH_4 and MgBr_2 (eq. 36) [24]. When we carried out this reaction, we



found the product to be BrMgAlH_4 and subsequent additions of excess LiAlH_4 did not result in the replacement of the final bromine atom (eq. 37) [28]. However, the reaction of NaAlH_4 with MgCl_2 in THF did produce $\text{Mg}(\text{AlH}_2)_2$ in quan-

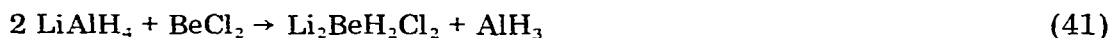


titative yield (eq. 38). Although the previously reported $\text{Mg}(\text{AlH}_2)_2$ was said to be soluble in Et_2O and decompose at 140°C , the $\text{Mg}(\text{AlH}_2)_2$ we prepared was insoluble in Et_2O and decomposed at 180°C . Furthermore, we were able to show that $\text{Mg}(\text{AlH}_2)_2$ in the presence of LiBr (see eq. 36) quickly forms BrMgAlH_4 (eq. 39), thus $\text{Mg}(\text{AlH}_2)_2$ could not have been formed in the presence of LiBr as reported earlier. Subsequent studies indeed show that $\text{Mg}(\text{AlH}_2)_2$ is insoluble

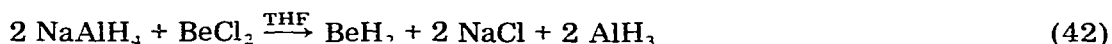


in all solvents tested, but still is an excellent reducing agent toward organic substrates [29].

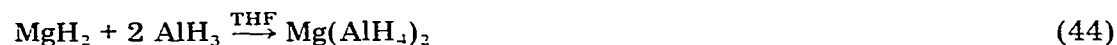
The situation with $\text{Be}(\text{AlH}_2)_2$ was not so different from the case of $\text{Mg}(\text{AlH}_2)_2$. It was reported that $\text{Be}(\text{AlH}_2)_2$ was prepared from LiAlH_4 and BeCl_2 in ether (eq. 40) and that it was found to be soluble in ether [25]. We repeated this reaction a number of times and found that under no conditions could we detect $\text{Be}(\text{AlH}_2)_2$ [29]. Instead, an insoluble solid was formed ($\text{Li}_2\text{BeH}_2\text{Cl}_2$) leaving AlH_3 in solution (eq. 41). The solid product, $\text{LiBeH}_2\text{Cl}_2$, was shown by X-ray powder



patterns and vacuum DTA-TGA studies, not to be a mixture of BeH_2 and 2 LiCl . When the reaction was carried out with NaAlH_4 , similar results were obtained except that BeH_2 and 2 NaCl did not interact to form a complex (eq. 42).

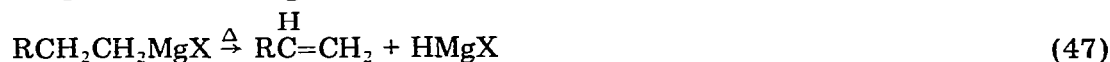
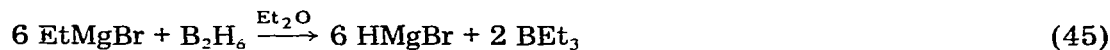


Maybe the most convincing experiments carried out showed that BeH_2 and AlH_3 in THF do not interact to form $\text{Be}(\text{AlH}_2)_2$, although under the same conditions MgH_2 and AlH_3 do interact to form $\text{Mg}(\text{AlH}_2)_2$ (eqs. 43, 44).



At about the same time as the above work we were also trying to prepare HMgX compounds (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$) in order to test them as stereoselective reducing agents. Several workers [30] had already used these compounds(?) for

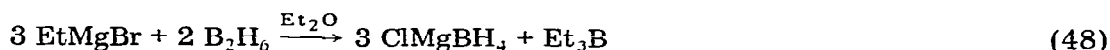
specific reductions not knowing very much about the integrity of these new reagents. The HMgX compounds were reported to have been prepared by three different methods (eqs. 45–47).



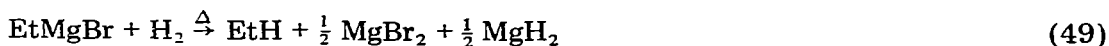
The reaction of EtMgBr with diborane in ether was reported to form HMgBr · 2 Et₂O [26]. This compound was reported to form the mono etherate, HMgBr · Et₂O, when the bis-etherate was heated to 200°C. The HMgX compounds were also reported prepared in THF as the bis-THF etherates. Contrary to this report was another one involving the hydrogenolysis of Grignard reagents (eq. 46) to form the HMgX compounds as monoetherates [31]. This same report stated that HMgX compounds disproportionate to MgH₂ and MgX₂ at temperatures above 125°C or when the etherate was placed in THF, facts contrary to the above report. The significance of the third report involving the pyrolysis of Grignard reagents (eq. 47) [32] was somewhat questioned since the analysis of the product of heating EtMgBr to 200°C was reported to be H : Mg : Br = 1.00 : 1.00 : 1.00 (a rather rare analytical result for such sensitive compounds). Of more significance was the fact that the X-ray diffraction of this unsolvated product was different from that of unsolvated MgH₂ and MgBr₂ · OEt₂, thus causing the claim the product (HMgBr) was not a physical mixture of MgH₂ and MgBr₂.

After repeating all three of the methods of preparation of HMgX compounds, we concluded that none of these methods produced true HMgX compounds. Our conclusion was based on the following facts.

Although the reaction of EtMgX compounds (where X = Cl, Br, I) with diborane in ether and THF was reported to form HMgCl, HMgBr, and HMgI as the bisetherates [26] in our hands this reaction took an entirely different course [33]. Under a variety of conditions we never obtained even a trace of HMgX compounds, but rather a mixture of ClMgBH₄ and Et₃B (eq. 48).



When we repeated the hydrogenolysis work [31], we found that in ether where X = Br or I, an insoluble precipitate was always formed (MgH₂) and the solutions contained the ether soluble MgBr₂ or MgI₂ (eq. 49) [34]. Although the prior art reported that the solid residue was an insoluble precipitate of



the HMgX compound as the mono etherate, we observed no halogen in the product. The prior art reported that the HMgX compounds formed on hydrogenolysis of Grignard reagents disproportionate to MgH₂ and MgX₂ when heated above 125°C or treated with THF, however, these reports are contrary to the reports of the product formed from diborane and Grignard reagent.

The third method involving the pyrolysis of EtMgBr (eq. 47) determined that

the product of the reaction was HMgBr and not a physical mixture of MgH₂ and MgBr₂, because the powder diffraction patterns were different [32]. However, we made the same product by pyrolysis of EtMgBr and found the empirical formula to be HMgBr · 0.27 Et₂O. When we compared the X-ray powder diffraction data of this product with that of individual samples of MgH₂ and MgBr₂ · 0.27 Et₂O, we found the powder patterns to be the same [33]. The original difference in powder pattern data was due to the failure to compare MgBr₂ with the correct amount of solvated ether with the so called HMgBr. The conclusion, of course, is that HMgBr was not formed, but only a physical mixture of MgH₂ and MgBr₂. Thus we were not able to verify any of these reports for the preparation of HMgX compounds.

We have, however, more recently prepared HMgBr and HMgCl by redistribution of MgH₂ and MgX₂ in THF, (eq. 50) [35]. Both HMgBr and HMgCl are



soluble in THF, stable to disproportionation in THF and insoluble in ether. Since MgH₂ is very insoluble in THF, it is clear that compound formation takes place. Infrared spectroscopy established the formation of Mg—H bonds and the nature of the dimer formed.

After this initial experience with so much conflicting information, we set out to study fundamental systems very carefully so that main group metal hydride chemistry could be put on a solid trustworthy footing. Because we plodded through some of the confusion that existed in the early days in this area, latter progress has been much more rapid and speculation concerning unknown systems more accurate. The past few years have been satisfying indeed and we have already realized a number of our goals in this area of chemistry. In this respect, we have managed to prepare (mainly through the efforts of two extraordinary coworkers, John Watkins and Anil Goel) a number of new complex metal hydrides where the central metal atom is copper, zinc, and magnesium. Some representative new hydrides are as follows: LiCuH₂ [36], Li₂CuH₅ [37], LiZnH₃ [38], LiMgH₃ [39], LiMg₂H₅ and MgZnH₄ [40]. We have also prepared a number of new simple metal hydrides which have turned out to be excellent stereoselective reducing agents, e.g. HMgOR compounds [41], HMgNR₂ compounds [42], H₂AlX compounds (where X = I, OR and NR₂) [43] and H₂BX compounds (where X = I, OR and NR₂) [43]. We have also studied the mechanistic pathways of a number of reactions in this area in an attempt to establish the nature of the fundamental chemistry concerning main group metal hydrides.

This work in its entirety (1965—1976) was generously supported by the Office of Naval Research for which I am very grateful. I am also grateful that I have had a number of superb students and postdoctoral associates working in this area who are indeed responsible for the difficult experimental work. The students who worked in this area were: Rob Sanders, Bob Beach, Dick Schwartz and John Watkins and the postdoctoral associates were Dr. Bruce James, Dr. Joseph Dilts, Dr. Roger Kovar, Dr. Ted Korenowski, Dr. Hari Prasad, and Dr. Anil Goel. Also I was blessed for one year by the presence of Dr. Pierre Claudy from CNRS in Lyon who proved to be a remarkable researcher. To be associated with such colleagues adds more understanding to

the biblical passage, "Give thanks to the Lord for He is good and His mercy is everlasting" (Psalm 107).

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