dynamic Jahn–Teller distortions of a ^3E ground state, tungstenocene bears a closer resemblance to the orbitally nondegenerate metallocenes. Both metallocenes exhibit intense charge-transfer bands in the near-UV, but tungstenocene shows an additional sharp electronic transition at ~3240 cm^{-1}, which is assigned to a transition between two spin–orbit substates. We conclude that Jahn–Teller activity of tungstenocene is quenched by spin–orbit coupling.

A substantial fraction of the expelled ligands CO and C_2H_4 stays within the same matrix cage as the metallocene, resulting in mutual perturbation of IR and UV spectra. On annealing these expelled ligands diffuse away without recombining. However, both heavy metallocenes (M = Mo, W) react thermally with CO in the 50–65 K region in a Xe matrix. All the group 6 metallocenes react photochemically with CO to give the carbonyls MCp_2CO.

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Note Added in Proof. Since submitting this manuscript, we have conducted magnetic circular dichroism experiments on MCp_2 (M = Mo, W) in matrices. The resulting spectra show an intense *C* term, thus confirming that these metallocenes are paramagnetic. Details will be published elsewhere.

Registry No. WCp_2H_2, 1271-33-6; WCp_2D_2, 11082-26-1; $WCp_2(CH_3)H$, 72415-89-5; $WCp_2(C_2H_4)$, 37343-06-9; WCp_2CO, 39333-44-3; $MoCp_2H_2$, 1291-40-3; $MoCp_2D_2$, 11082-25-0; $MoCp_2CO$, 12701-85-8; $W(\eta\text{-}C_5D_5)_2H_2$, 82482-36-8; $W(\eta\text{-}C_5D_5)_2D_2$, 82482-37-9; $Mo(\eta\text{-}C_5D_5)_2H_2$, 82482-38-0; $Mo(\eta\text{-}C_5D_5)_2D_2$, 82482-39-1; WCp_2, 51481-44-8; $MoCp_2$, 51370-80-0; VCp_2, 1277-47-0; $CrCp_2$, 1271-24-5; CH_4, 74-82-8; CO, 630-08-0; C_2H_4, 74-85-1; Ar, 7440-37-1.

Supplementary Material Available: Sublimation temperatures (Table I) and frequency listings (Tables II–VII) (7 pages). Ordering information is given on any current masthead page.

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Addition Compounds of Alkali Metal Hydrides. 22. Convenient Procedures for the Preparation of Lithium Borohydride from Sodium Borohydride and Borane–Dimethyl Sulfide in Simple Ether Solvents

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The preparation of $LiBH_4$ in various ether solvents from the readily available reagents $NaBH_4$ and lithium halides is described. The reactivity of lithium halides toward the metathesis reaction generally follows the order LiBr > LiI > LiCl. The heterogeneous reactions proceed satisfactorily with vigorous magnetic stirring. However, attempting to increase the scale of the preparations utilizing mechanical stirrers resulted in incomplete reactions and decreased yield. On the other hand, when the heterogeneous mixture was stirred with mechanical stirrers fitted with Teflon paddles and a mass of glass beads, the rate of the reaction increased considerably, producing quantitative yields of $LiBH_4$ in greatly decreased reaction times. The ease of conversion of $NaBH_4$ into $LiBH_4$ in various solvents follows the order isopropylamine > 1,3-dioxolane > monoglyme > tetrahydrofuran ≈ ether. The isolation of solvent-free $LiBH_4$ from the various solvates was attempted under different conditions. In most cases, normal distillation at 100 or 150 °C produced a strong 1:1 solvate, $LiBH_4\cdot$solvent. Only in the case of ethyl ether is the solvent of solvation readily removed at 100 °C at atmospheric pressure. In the other cases, both higher temperatures, up to 150 °C, and lower pressures, down to 0.1 mm, are required to produce the unsolvated material. Thus the ease of isolating unsolvated $LiBH_4$ is ethyl ether > IPA > THF > 1,3-D ≈ MG. Consequently, ethyl ether is the medium of choice for the preparation of $LiBH_4$ by the metathesis of $NaBH_4$ and LiBr. $LiBH_4$ can also be conveniently prepared by the reaction of LiH with $H_3B\cdot SMe_2$ in ethyl ether. Dimethyl sulfide is readily removed, along with ethyl ether of solvation, at 100 °C (atmospheric pressure). These procedures make $LiBH_4$ readily available.

Lithium borohydride is a selective and more reactive reducing agent than sodium borohydride, much more soluble in a variety of organic solvents than the sodium salt. It was first made on a small scale by the action of gaseous diborane or aluminum borohydride on ethyllithium in benzene solutions (eq 1 and 2).[2] Alternatively, in the presence of diethyl ether,

$$3LiC_2H_5 + 2B_2H_6 \rightarrow 3LiBH_4 + (C_2H_5)_3B \tag{1}$$

$$3LiC_2H_5 + Al(BH_4)_3 \rightarrow 3LiBH_4 + (C_2H_5)_3Al \tag{2}$$

diborane is quantitatively absorbed by lithium hydride with the formation of the monoetherate of lithium borohydride in a state of high purity[3] (eq 3).

$$2LiH + B_2H_6 + 2(C_2H_5)_2O \xrightarrow{Et_2O} 2LiBH_4\cdot Et_2O \tag{3}$$

Sodium borohydride is currently manufactured on a large scale and is a comparatively economical reagent. On the other hand, the cost of lithium borohydride is prohibitive for normal application in preparative reductions. Hence, it is desirable to have a convenient procedure to convert sodium borohydride into lithium borohydride.

The first synthetic procedure for the preparation of lithium borohydride by metathesis was reported by Schlesinger, Brown, and Hyde.[4] The reaction of sodium borohydride and lithium chloride was carried out in isopropylamine under reflux for 3 h (eq 4). (Both sodium borohydride and lithium chloride

$$NaBH_4 + LiCl \rightarrow LiBH_4 + NaCl \tag{4}$$

are soluble in isopropylamine.) It was difficult to remove

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(1) Postdoctoral research associates on Grant ARO-DAAG-29-79-C-0027, supported by the U.S. Army Research Office.

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Table I. Solubilities of Various Metal Borohydrides and Salts (M) in Organic Solvents at 25 °C[a]

	solvent				
reagent	isopropylamine	monoglyme	1,3-dioxolane	tetrahydrofuran	diethyl ether
$NaBH_4$	1.10	0.15	0.02	0.02	insol
NaCl	insol	insol	insol	insol	insol
NaBr		insol	insol	insol	insol
$LiBH_4$	1.27	1.9 (0 °C)	1.75 (0 °C)		
		4.7	1.99	11.43	1.40
		2.1 (75 °C)			3.04 (34 °C)
LiCl	1.42	0.44	0.59	0.61	1×10^{-4}
		0.10 (75 °C)		>1.00 (0 °C)	
LiBr		1.67	>1.00	3.96	1.05
LiI					>1.00
LiH	insol	insol	insol	insol	insol
BMS	sol	sol	sol	sol	sol

[a] Unless otherwise indicated.

isopropylamine of solvation, but a high yield (94%) of an unsolvated $LiBH_4$ was obtained. Later, Subba Rao examined the reaction of $NaBH_4$ with LiCl in monoglyme (MG). The reaction proceeded slowly, but satisfactorily, but pure unsolvated $LiBH_4$ could not be isolated.[5] Monoglyme holds on tenaciously to the salt. Snover also examined the reaction of $NaBH_4$ and LiCl in various solvents such as MG, tetrahydrofuran (THF), and EE.[6] The reactions were quite sluggish. Three days at 25 °C were required for complete conversion to $LiBH_4$ in MG. Only 35% of $LiBH_4$ was formed in refluxing THF in 1 day, and no reaction was observed in EE over several hours. However, Paul and Joseph successfully achieved the synthesis of $LiBH_4$ in THF, using the reaction between KBH_4 and LiCl.[7] The metathesis reaction between $NaBH_4$ and LiCl appeared to proceed readily in alcohol.[8] Unfortunately, $LiBH_4$ undergoes fairly rapid hydrolysis in the alcohol solvents and it is not possible to isolate the salt.[9]

In view of the long-standing problem of achieving a quantitative conversion of $NaBH_4$ into $LiBH_4$ under conditions that would permit isolation of unsolvated $LiBH_4$, it appeared desirable to renew exploration of this reaction. We finally were successful in achieving a convenient procedure for the conversion of $NaBH_4$ into $LiBH_4$ in ether and THF.[10] We wish to report here our complete studies on this metathesis reaction using various lithium salts in appropriate solvents, solvents that are commonly used for organic reductions.

Results and Discussion

Solubility. The lithium salts such as LiCl, LiBr, and LiH and various solvents such as isopropylamine (IPA), EE, THF, 1,3-dioxolane (1,3-D), and MG were selected as representative lithium salts and organic solvents to be examined. The rate of the metathesis reaction and recovery of $LiBH_4$ are very much affected by the solubility of the reactants and products. Hence, the solubilities of various metal borohydrides and metal salts in these organic solvents were examined. The results are summarized in Table I. The data indicate that the reaction mixtures are invariably heterogeneous. Nevertheless, since the product, $LiBH_4$, is highly soluble in all of these solvents and sodium halide, the other product, is practically insoluble, solutions of $LiBH_4$ can be conveniently recovered by mere filtration of the reaction mixtures. The rate and stoichiometric studies are given below.

General Procedure for Rate and Stoichiometry Studies. The reactions were carried out under a nitrogen atmosphere at the desired reaction temperatures (0 °C, 25 °C, and reflux temperature). In a typical procedure, the lithium halide (0.8–1.0 M) was treated with $NaBH_4$ (0.8–1.0 M) dissolved (IPA) or suspended in an appropriate solvent. (Amounts of $NaBH_4$ and LiX were used to provide solutions of the indicated molarity, had the materials dissolved.) The rate of the reaction was followed by removing clear aliquots, obtained by centrifuging the reaction mixture at appropriate time intervals, and analyzing them by the hydrolysis method, with the exception of the reaction in IPA,[11] where the reactants were soluble. The results are summarized in Table II.

General Procedure for the Isolation of Unsolvated $LiBH_4$. $NaBH_4$ was treated with LiX in an appropriate solvent. After the completion of the reaction, the NaX settled down. The clear solution of $LiBH_4$ was obtained by using a double-ended needle or by filtering the reaction mixture. A known amount of $LiBH_4$ (100 mmol) solution was taken for isolating the solvent-free salt. Removal of the solvent was studied by (1) normal distillation at 100 and 150 °C (atmospheric pressure, 748 mmHg) and (2) removal of the excess solvent using aspirator vacuum and then heating of the residue at 100 and 150 °C under reduced pressure (0.1 mmHg). The removal of solvent was monitored by weighing the residue until a constant weight was obtained. From the weight, the composition of the solvate was calculated. The results are given in Table III. The nature of the $LiBH_4$·solvent complex and the optimum condition necessary for obtaining the unsolvated $LiBH_4$ are presented in Table IV.

Preparation of $LiBH_4$ in Isopropylamine. The procedure reported by Schlesinger, Brown, and Hyde[4] was earlier used by Metal Hydrides, Inc., for the preparation of $LiBH_4$. However, they encountered difficulties in obtaining pure $LiBH_4$ by this procedure. Consequently, we decided to reexamine this synthesis. The reaction in isopropylamine is homogeneous, since both $NaBH_4$ and LiCl are soluble in isopropylamine (Table I). The reaction was reasonably fast, producing $LiBH_4$ in a yield of 97% in 8 h at 25 °C and 100% in 2 h at reflux temperature (35 °C). White solid NaCl formed and precipitated. Filtration of the reaction mixture provided a clear solution of $LiBH_4$ (1.15 M). Unsolvated $LiBH_4$ was isolated from 87 mL of $LiBH_4$ (1.15 M, 100 mmol, 2.2 g) in IPA as described above. Distillation of IPA at 100 °C (748 mmHg) resulted in the removal of 73.4 mL of IPA in 1 h. The weight of the residue (viscous liquid) corresponded to $LiBH_4$·1.6IPA. Further removal of solvent was quite difficult, with the residue containing 0.8 mol of solvent/$LiBH_4$, even after 8 h. Similarly, after 8 h at 150 °C, the residue was $LiBH_4$·0.55IPA. However, under reduced pressure (0.1 mmHg), unsolvated $LiBH_4$ was obtained in 1 h at 100 °C and in 30 min at 150 °C: mp 277–279 °C dec (lit.[10] mp 278–279 °C dec); ^{11}B NMR δ −41.78 (quintet) with respect to $BF_3 \cdot OEt_2$ (δ 0).

Preparation of $LiBH_4$ in Ether. No significant reaction was observed between $NaBH_4$ and LiCl vigorously stirred magnetically as suspensions in ethyl ether at 25 °C or at reflux temperature (35 °C). Both salts are essentially insoluble in this solvent, and this evidently provides a major hurdle for the metathesis reaction. On the other hand, LiBr and LiI are soluble in EE (Table I). Indeed, these reactions proved much more favorable, proceeding to essential completion in 48 h at 25 °C (eq 5). At reflux, the reactions appeared to be essentially complete in 32 h. The bromide appeared to be slightly

$$NaBH_4 + LiBr \xrightarrow[48\ h]{25\ °C,\ EE} \underset{100\%}{LiBH_4} + NaBr\downarrow \qquad (5)$$

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Table II. Synthesis of Metal Borohydrides by Metathesis[a] and Reaction of Lithium Hydride with Borane-Dimethyl Sulfide

borohydride	salt	solvent	temp, °C	stirring[b]	% reacn 1 h	4 h	8 h	16 h	24 h	48 h
$NaBH_4$	LiCl	IPA	25	A			97			
$NaBH_4$	LiCl	IPA	34	A	100[c]					
$NaBH_4$	LiCl	IPA	34	B	97[c]					
$NaBH_4$	LiCl	EE	35	A	3		3		4	7
$NaBH_4$	LiCl	EE	35	C	21		25		26	
$NaBH_4$	LiBr	EE	25	A	3		3	29	79	100
$NaBH_4$	LiBr	EE	35	A	3		9	76	89	99[d]
$NaBH_4$	LiBr	EE	35	B	2		4		6	
$NaBH_4$	LiBr	EE	35	C	8	74[e]		98[f]		
$NaBH_4$	LiI	EE	35	A	4	15	25		62	87
$NaBH_4$	LiCl	THF	25	A					7	21
$NaBH_4$	LiCl	THF	25	B			3		3	
$NaBH_4$	LiCl	THF	25	C	9		47		100	
$NaBH_4$	LiCl	THF	67	A					31	65
$NaBH_4$	LiCl	THF	67	B	2		12		17	
$NaBH_4$	LiCl	THF	67	C	25[c]	52	100[g]			
$NaBH_4$	LiBr	THF	25	A	2		11	53	62	81
$NaBH_4$	LiBr	THF	25	B		3	10[g]		14	
$NaBH_4$	LiBr	THF	25	C	14	32	45		83	97[d]
$NaBH_4$	LiBr	THF	67	A	37		92	99		
$NaBH_4$	LiBr	THF	67	B	7	35	68		90	
$NaBH_4$	LiBr	THF	67	C	52	90	100			
KBH_4	LiCl	THF	25	A		100				
KBH_4	LiCl	THF	25	C	100[c]					
$NaBH_4$	LiCl	1,3-D	25	A					30	57
$NaBH_4$	LiCl	1,3-D	74	A					20	44[i]
$NaBH_4$	LiCl	1,3-D	25	C	10	32	54	73[f]	100	
$NaBH_4$	LiBr	1,3-D	25	A	24		69	83	87	92
$NaBH_4$	LiBr	1,3-D	74	A	12		31	44	51	58
$NaBH_4$	LiBr	1,3-D	25	C	53	72	84	93[f]	100	
$NaBH_4$	LiCl	MG	0	A	12[c]		29		41	
$NaBH_4$	LiCl	MG	25	A	33	34	36		49	94[j]
$NaBH_4$	LiCl	MG	25	C	20	25	33		73	
$NaBH_4$	LiCl	MG	85	A	42[c]	46	56		68	
$NaBH_4$	LiBr	MG	25	A	6[c]	13	24		47	
$NaBH_4$	LiBr	MG	85	A	2	4	12		76	99[i]
$NaBH_4$	LiBr	MG	25	C	9	54	80	99		
$BH_3 \cdot S(CH_3)_2$[k]	LiH	EE	25	A				100		
$BH_3 \cdot S(CH_3)_2$[k]	LiH	EE	35	A			100			

[a] A 100-mmol quantity of sodium or potassium borohydride stirred in 100 mL of ethyl ether (EE) or tetrahydrofuran (THF) with 1 equiv of salt. [b] Stirring: A, magnetic stirrer; B, overhead mechanical stirrer; C, overhead mechanical stirrer with Teflon paddle and 25% by volume of 6-mm glass beads. [c] 2 h. [d] 32 h. [e] 6 h. [f] 12 h. [g] 10 h. [h] 5 h. [i] 36 h. [j] 72 h. [k] 150 mmol of LiH. The reaction was monitored by ^{11}B NMR.

more favorable than the iodide. Consequently, we concentrated our efforts on the bromide.

Although the problem had apparently been solved, we encountered an unexpected difficulty.[12] These experiments had been carried out on a 100-mmol scale, with a magnetic stirrer. However, attempts to carry out these reactions on a larger scale, using a mechanical stirrer, resulted in a serious decrease in the conversions, both in our laboratory and at Aldrich-Boranes, Inc.[12] Indeed, on the same scale as the previous experiments, substituting mechanical stirring for magnetic stirring, we achieved in refluxing ethyl ether only 6% reaction in 24 h, as compared to 89% for the corresponding procedure using magnetic stirring. It appeared that the rapidly moving magnetic stirring bar must be producing an abrasion of the surface of $NaBH_4$ that was highly beneficial for the reaction.

Accordingly, we attempted to introduce such abrasion in a mechanical system by adding 6-mm glass beads to a mechanically stirred system containing a Teflon paddle. This modification not only solved the problem but actually improved the rate of reaction. In refluxing ethyl ether, the reaction of LiBr with $NaBH_4$ proceeded to completion in 12 h (compare eq 5). It should be pointed out that the use of ball mills to produce a grinding action on heterogeneous reaction mixtures is not new.[13,14] However, such ball mills generally have only small capacities, whereas, the use of a suitable mechanical stirrer with glass beads is capable of large scale-up. Indeed, in the present case, this device made possible the simple synthesis in ether solvents of $LiBH_4$ from $NaBH_4$ on a relatively large scale.

Distillation of a solution of $LiBH_4$ in ether (81.3 mL, 1.23 M, 100 mmol, 2.2 g) at 100 °C produced a residue in 30 min, weighing 2.22 g, indicating the quantitative removal of the solvent. Alternatively, ether could be removed completely at 25 °C in 1–2 h, with a vacuum of 0.1 mm. The results are given in Table III.

We experienced no difficulty in carrying out these preparations of $LiBH_4$ in ether on an increased scale of 0.5 mol. Similarly, we experienced no difficulty in isolating solid $LiBH_4$ in essentially quantitative yield from these solutions.

Preparation of $LiBH_4$ in THF. Both LiCl and LiBr are soluble in THF. However, using LiCl and $NaBH_4$ in refluxing THF, Snover obtained only a 35% yield of $LiBH_4$ in 24 h. We observed that, using magnetic stirring, the reaction required 96 h for completion. With LiBr, the reaction was considerably faster, proceeding to 99% completion in 16 h under the same conditions. Here also, the use of glass beads and the mechanical stirrer with a Teflon paddle in these reactions enhanced the rate considerably. Thus, at reflux temperature,

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Table III. Removal of Solvent of Crystallization from $LiBH_4$·Solvent Complex

solvent	temp, °C	pressure, torr	solvent present[a]				
			initial[b]	0.5 h	1 h	4 h	8 h
IPA	100	748	1.6	1.32	1.1	0.92	0.8
IPA	150	748	1.4	1.07	0.98	0.80	0.55
IPA	25	0.1	1.3	1.12	1.01	0.9	0.8
IPA	100	0.1	1.2	0.10	0.02		
IPA	150	0.1	1.21	0.02			
EE	100	748		0.00			
EE	150	748		0.00			
EE	25	0.1	1.0	0.15	0.06	0.00[c]	
THF	100	748	1.2		1.0	0.87	0.76
THF	150	748	1.1		0.9	0.76	0.62
THF	25	0.1	1.05	0.98	0.95	0.9	0.88
THF	100	0.1	1.01	0.4	0.19	0.02	0.02
THF	150	0.1	1.02	0.25	0.04	0.04	
1,3-D	100	748	1.12	1.05	0.98	0.90	0.81
1,3-D	150	748	1.08		0.95	0.83	0.73
1,3-D	25	0.1	1.05		1.0	0.96	0.92
1,3-D	100	0.1	0.99	0.38	0.24	0.06	0.03
1,3-D	150	0.1	0.98	0.27	0.09	0.03[c]	
MG	100	748	1.01	0.98	0.96	0.92	0.89
MG	150	748	0.99		0.94	0.88	0.80
MG	25	0.1	1.02	0.97	0.95	0.93	0.9
MG	100	0.1	1.0	0.51	0.44	0.28	0.16
MG	150	0.1	1.01	0.47	0.26	0.02[c]	0.02

[a] mmol per mmol of $LiBH_4$. [b] Corresponds to the residues obtained after removal of solvent by distillation or under aspirator vacuum. [c] 2 h.

Table IV. Summary of the Isolation of Unsolvated $LiBH_4$[a]

solvate[b]	mp, °C	temp, °C/pressure, torr/time for desolvation, h	% purity
$LiBH_4$·1.6IPA[c]		100/0.1/1	98
$LiBH_4$·Et_2O	274-277 dec[d]	100/748/0.5	100
$LiBH_4$·THF	38-40	150/0.1/1.0	96
$LiBH_4$·1,3-D	235-239	150/0.1/2.0	97
$LiBH_4$·MG	64-67	150/0.1/2.0	98

[a] 100 mmol of $LiBH_4$ in the solvent was used. [b] Solvate obtained after removal of solvent under aspirator vacuum at 25 °C. [c] Solvate obtained after a simple distillation at 100 °C. [d] Melting point of unsolvated $LiBH_4$.

the reaction with LiCl was complete in 10 h while that with LiBr was complete in 8 h. Paul and Joseph[7] used KBH_4 and LiCl in THF at 25 °C, the conversion being complete in 8 h. However, we found that the same reaction was complete in 4 h, with a magnetic stirrer, and in 2 h, using a mechanical stirrer with glass beads (eq 6).

$$KBH_4 + LiCl \xrightarrow[2\ h]{THF,\ 25\ °C} \underset{100\%}{LiBH_4} + KCl\downarrow \qquad (6)$$

THF forms a strong complex with $LiBH_4$. Thus, a removal of solvent from 77.5 mL (1.29 M, 100 mmol) of $LiBH_4$ in THF at 100 and 150 °C for 8 h resulted in the formation of $LiBH_4$·0.7THF and $LiBH_4$·0.60THF, respectively. However, desolvated $LiBH_4$ could be obtained by heating the solvated complex under vacuum for 4 h at 100 °C and 1 h at 150 °C. In some trial runs under these conditions, only 78% pure $LiBH_4$ was obtained. Although this corresponds to $LiBH_4$·0.22THF, it is more likely that a small quantity of moisture present in THF might have hydrolyzed $LiBH_4$ to $LiB(OH)_4$. Because of the large difference in molecular weights, a small amount of the hydrolyzed impurity would cause a large change in the apparent purity of the $LiBH_4$. The complete removal of THF has been confirmed by repeating the process with a known amount of $LiBH_4$ and freshly distilled THF. The results are given in Tables III and IV.

Preparation of $LiBH_4$ in 1,3-Dioxolane. 1,3-Dioxolane is available commercially. It is an economical solvent. We have established that $NaBH_4$ is slightly soluble and both LiCl and LiBr are easily soluble in the solvent (Table I). The reaction with LiCl using magnetic stirring proceeded very slowly at 25 °C, providing 99% of the product in 7 days. On the other hand, LiBr reacted faster at 25 °C, giving 92% of $LiBH_4$ in 2 days. These reactions were also facilitated when the reaction mixtures were stirred mechanically in the presence of glass beads. Essentially quantitative conversion was observed in 24 h at 25 °C. NaCl or NaBr precipitated as a finely divided solid. Filtration of the mixture gave a clear solution.

Unfortunately, isolation of solvent-free $LiBH_4$ requires drastic conditions. Complete removal of 1,3-D could not be achieved by normal distillation at 100 and 150 °C (Table III). (The residue corresponded to the 1:1 complex, $LiBH_4$·1,3-D, mp 235–239 °C.) However, complete removal of solvent could be achieved by heating the 1:1 $LiBH_4$·solvent complex under reduced pressure (0.1 mmHg) for 4–8 h at 100 °C or 2–3 h at 150 °C (Table III).

Preparation of $LiBH_4$ in Monoglyme. Both $NaBH_4$ and LiCl have modest solubility in MG (Table I). Although Subba Rao had prepared the $LiBH_4$ in solution in MG from $NaBH_4$ and LiCl, he failed to obtain pure unsolvated $LiBH_4$ from the solution.[5] Hence, we undertook to restudy this reaction. LiCl reacted very slowly, even at reflux temperature, and the conversions were incomplete. However, reaction of $NaBH_4$ with LiBr proceeded more readily at reflux, providing a quantitative yield of $LiBH_4$ in 2 days. On the other hand, the reaction was complete in 16 h at 25 °C when the reaction mixture was subjected to the grinding effect introduced by the mechanical stirrer and glass beads. The results are given in Table II.

The sodium salts precipitated as a white solid. Filtration provided a clear solution. Removal of the solvent by normal distillation provided a 1:1 complex, $LiBH_4$·MG, as white crystals: mp 64–67 °C. Desolvation of the complex required drastic conditions. Thus, heating the 1:1 complex at 150 °C for 4–8 h under 0.1 mmHg pressure produced solvent-free $LiBH_4$. The data are given in Tables III and IV.

The results indicate that generally the reactivity of lithium halides follows the order LiBr > LiI > LiCl. The ease of conversion of $NaBH_4$ into $LiBH_4$ in various solvents follows the order IPA > 1,3-D > MG > THF ≈ EE. However, the facility of isolating unsolvated $LiBH_4$ is EE > IPA > THF > 1,3-D ≈ MG.

Preparation of $LiBH_4$ from BMS and LiH in EE. Diborane is known to react with LiH in EE at −80 °C, producing an essentially quantitative yield of $LiBH_4$ in 3–4 h.[4] However, the safe handling of gaseous diborane requires special equipment. On the other hand, borane–dimethyl sulfide (BMS) is a stable, neat liquid, commercially available. Hence, it appeared desirable to explore the preparation of $LiBH_4$ in EE using BMS. The reaction was relatively slow at 25 °C, requiring 16 h for completion. However, under reflux, a quantitative conversion was obtained in 8 h. Excess LiH settled down, giving a clear solution of $LiBH_4$ in EE. The clear solution was transferred by a double-ended needle into a second weighed flask. A simple distillation at 100 °C (748 mmHg) removed both ethyl ether and dimethyl sulfide, providing a 98% yield of 100% pure $LiBH_4$ (Table III).

Properties of $LiBH_4$. Finely divided lithium borohydride is known to flash upon exposure to humid air, and hence transfer of the solid should be manipulated in a dry-nitrogen atmosphere.[15] However, solutions of $LiBH_4$ are relatively insensitive to moisture.

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[15] Nystrom, R. F.; Chaikin, S. W.; Brown, W. G. *J. Am. Chem. Soc.* **1949**, *71*, 3245.

$LiBH_4$ isolated from the $LiBH_4$·IPA complex showed a melting point of 276–278 °C with decomposition (lit.[10] mp 275–278 °C dec). ^{11}B NMR showed a quintet centered around −41.8 ppm in THF.

The $LiBH_4$·MG complex is very soluble in THF and 1,3-dioxolane but slightly soluble in EE. The melting point of the complex is 64–67 °C (lit.[6] mp 65–67 °C): ^{11}B NMR δ −41.8 (q) in THF. The unsolvated $LiBH_4$ prepared from the MG solvate melts at 277–279 °C dec.

The $LiBH_4$·1,3-D complex is very soluble in THF but slightly soluble in EE. The complex melts at 235–239 °C: ^{11}B NMR (THF) δ −41.74 (q). However, the physical constants of desolvated $LiBH_4$ are identical to the literature data: mp 274–277 °C dec; ^{11}B NMR δ −42.0.

The $LiBH_4$·THF complex was soluble in 1,3-dioxolane but slightly soluble in EE. The characteristics of this complex are as follows: mp 38–40 °C; ^{11}B NMR (THF) δ −41.75.

Conclusion

This study describes the facile conversion of $NaBH_4$ into $LiBH_4$ by the metathesis reaction with lithium halides in selected aprotic solvents. Vigorous magnetic stirring facilitates the conversions. Moreover, introduction of glass beads into the mechanically stirred reaction mixtures enhances the rates of reaction, facilitating the synthesis of $LiBH_4$ in simple ether solvents. Clear solutions of $LiBH_4$ can be easily separated from the precipitated sodium halides. Removal of solvent yields 1:1 complexes, $LiBH_4$·solvent. Conditions have been established for complete removal of solvents from the solvate. Ease of removal of solvent follows the order EE > IPA > THF > 1,3-D ≈ MG. Consequently, the metathesis reaction in ether affords a convenient, practical method for preparing solvent-free $LiBH_4$. Alternatively, the addition reaction between BMS and LiH in ether provides a convenient route for the synthesis of $LiBH_4$. This study establishes simple, economic routes for the preparation of $LiBH_4$. This development should enhance the utility of this reagent for selective reductions in organic synthesis.

Experimental Section

All of the chemicals used were commercial products of the highest purity and were purified just before use, if necessary.

Sodium borohydride and lithium borohydride (98% purity, Ventron) were used without further purification. LiCl, LiBr (Fisher Scientific Co.), and LiI (Ventron) were used after thoroughly heating to 120 °C under vacuum (0.1 mmHg) for 3–4 h.

The aprotic solvents such as MG, 1,3-D, and THF, distilled over a slight excess of lithium aluminum hydride, were stored under nitrogen. IPA was distilled over a slight excess of calcium hydride while thoroughly protected from moisture. Anhydrous EE, stored under molecular sieves, was used.

Hypodermic syringes and double-ended needles were used at all times to transfer materials.[16] All glassware was dried thoroughly in a drying oven at 125 °C for several hours, assembled quickly, and then cooled under a stream of nitrogen. All experiments were carried out under N_2.

Solubility. A saturated solution was prepared by stirring the salt with an appropriate solvent for several hours. The mixture was centrifuged or filtered to separate the excess of compound. The solubility of borohydride was determined by estimating an aliquot (1–2 mL) of the clear solution by hydrolysis. The solubility of other salts was determined by removing the solvent under reduced pressure from an aliquot (1–2 mL) of the salt solution and weighing the residue. The results are given in Table I.

General Procedure for Rate Determinations. In a typical experiment, a 250-mL round-bottom flask containing a magnetic stirring bar and an inlet for nitrogen atmosphere was equipped with a reflux condenser leading to an outlet for nitrogen gas. To the predried flask was added 105 mmol of lithium halide. The flask was again flushed with nitrogen, and 100 mL of solvent was introduced with a double-ended needle. After 2 min of stirring, 3.93 g (104 mmol) of sodium borohydride was introduced to the solution under nitrogen atmosphere. The reaction mixture was maintained at the appropriate temperature. About 1 mL of the reaction mixture was withdrawn at various time intervals and centrifuged, and 0.25 mL was analyzed. The reaction is complete when the concentration of the solution becomes 1.0 M.

In a similar way, the rate of the reaction using glass beads and mechanical stirrer was determined. The results are given in Table II.

General Procedure for the Isolation of $LiBH_4$. The isolation of solvent-free $LiBH_4$ was studied as follows. A solution of $LiBH_4$ (100 mmol) in the appropriate solvent was taken in a weighed flask fitted with a distillation set. The solvent was distilled at 100 °C and the residue weighed after cooling under a stream of nitrogen. The heating was continued and the residue weighed periodically. From the data, the amount of solvent per mole of $LiBH_4$ was determined.

The process was repeated at 150 °C under normal pressure. Since most of the solvates except ether could not be removed completely under these conditions, the procedure was repeated under high vacuum at 25, 100, and 150 °C. Periodical weighing of the residue indicated the time required for complete removal of the solvent. The data are given in Tables III and IV.

Stoichiometry of the Reaction of Sodium Borohydride with Lithium Halide Using Magnetic Stirring. The reaction in ether is representative. The procedure described under rate determinations was followed. After 48 h of stirring at 25 °C, the reaction mixture was stirred at 34 °C for 30 min. The completed reaction showed a separation between the clear solution of lithium borohydride and the sodium bromide as a white precipitate. The clear solution of lithium borohydride in diethyl ether was transferred by a double-ended needle into a weighed 250-mL flask. The flask was connected to a distillation setup and heated to distill off diethyl ether, with collection in a graduated cylinder until the temperature of the oil bath reached 100 °C and no more diethyl ether distilled. There was obtained 75 mL of diethyl ether and 2.52 g of unsolvated lithium borohydride. Thus, a quantitative yield of 97% pure lithium borohydride was obtained. The lithium borohydride exhibited a melting point of 276–279 °C dec (lit.[11] mp 275–278 °C dec). This was also confirmed by the ^{11}B NMR spectrum. The spectrum showed a quintet centered at −40.69 ppm in diethyl ether in relation to the reference BF_3·OEt_2, identical with the behavior of commerical $LiBH_4$.

Stoichiometry of the Reaction of Sodium Borohydride with Lithium Halide in Diethyl Ether Using Mechanical Stirring with Glass Beads. In a typical experiment, a three-necked, 2-L, round-bottom flask with side arm containing glass beads (6 mm diameter, 180 g, ~$^1/_4$ volume of the solvent), a mechanically operated Teflon paddle (9 cm in length), and an inlet for nitrogen was equipped with a reflux condenser leading to a bubbler outlet for the nitrogen gas. In the predried flask was placed 19.65 g (500 mmol) of $NaBH_4$ (98% pure, J. T. Baker Chemical Co.) and 45.6 g (525 mmol) of LiBr (99% pure, Matheson Coleman and Bell) under a nitrogen atmosphere. The flask was again flushed with nitrogen, and 500 mL of diethyl ether was introduced with a double-ended needle. The reaction was carried out at 25 °C with overhead stirring for 18 h and at 35 °C for 0.5 h. Insoluble sodium bromide is formed as a white solid and precipitated out completely. The clear solution of $LiBH_4$ in diethyl ether was transferred by a double-ended needle into a 500-mL volumetric standard flask. Approximately 350 mL was collected. An additional 50 mL of ether was added to the flask by a double-ended needle, and the flask was then maintained at reflux condition with stirring for 15 min. On cooling, a clear solution was observed above the NaBr precipitate. This solution was also transferred to the volumetric flask. The ether extraction of $LiBH_4$ from the precipitate was repeated twice, and the solutions were collected in the standard flask. The solution was made up to the mark, and the concentration of borohydride was determined to be 0.849 M by hydrolysis of a clear aliquot with a glycerine/H_2O/THF mixture for the hydrolysis.[12] The remaining slurry was filtered and the volume of the filtrate made up to 50 mL. The concentration of borohydride in this filtrate was found to be 0.50 M. Hence, the total recovery of $LiBH_4$ corresponds to 451 mmol (0.849 × 500 + 50 × 0.53) out of 500 mmol, a yield of 90%. Unsolvated $LiBH_4$ can be obtained as described above.

Registry No. $LiBH_4$, 16949-15-8; $NaBH_4$, 16940-66-2; KBH_4, 13762-51-1; BH_3·$S(CH_3)_2$, 13292-87-0; LiCl, 7447-41-8; LiBr, 7550-35-8; LiH, 7580-67-8; IPA, 75-31-0; EE, 60-29-7; THF, 109-99-9; 1,3-D, 646-06-0; MG, 110-71-4.

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(16) For details on these techniques, see ref 11, p 206.