stretching frequencies of the CrO_4^{3-} ion has been given.

This renews a problem which has not been always clearly understood and has contributed to many controversies and misunderstandings. Although it is essentially a spectroscopic problem, it is of great interest to many inorganic chemists dealing with oxoanions of the transition elements and those in unusual oxidation states in particular.

The fact that the $\nu_1(A_1)/\nu_3(F_2)$ frequency ratio for MO_4^{n-} species apparently shows erratic variations (for example, in the cases of VO_4^{3-}, WO_4^{2-}, or ReO_4^-, ν_1 lies at higher frequency than ν_3, whereas for MnO_4^-, CrO_4^{2-}, or RuO_4, the opposite behavior is observed) was the principal reason for the numerous misassignments made some time ago.

More than ten years ago, during a systematic investigation of the vibrational behavior of tetraoxometalates, we found that the variations of the ν_1/ν_3 frequency ratio could be correlated with the mass and the oxidation number of the central atom,[2,3] and we were also able to justify our findings with the aid of a very simple theoretical model.

The fact that these results have been published in a journal of restricted circulation has probably limited their diffusion, although they were included later in a review on the vibrational spectra of chalcogenometalates of the transition elements published in ref 4.

So that these results can be diffused definitively, the basic rules should be newly reformulated, as follows.

(1) For ions with the central atom belonging to the same group of the periodic system and possessing the same charge, the ratio ν_1/ν_3 increases with the mass of the central atom (for example, the ratio for ReO_4^- is larger than that for MnO_4^-).

(2) For a given central atom, the ν_1/ν_3 ratio grows with increasing charge of the anion (for example, it must be larger for CrO_4^{3-} than for CrO_4^{2-}, which are the species discussed in the paper of ref 1).

(3) For isoelectronic ions where the central atom mass remains approximately constant, the ratio ν_1/ν_3 increases with the increasing charge of the anion (for example, it is larger for WO_4^{2-} than for ReO_4^-).

(4) The ν_1/ν_3 ratio remains practically constant for ions of the same period and charge (for example, ν_1/ν_3 values are practically identical for CrO_4^{2-}, MnO_4^{2-}, and FeO_4^{2-}).

These rules can be extended to thio and seleno anions of the transition elements[3-5] and are also applicable to oxo and thio anions of the main-group elements.[6]

The fact that the well-known and widely used book of Nakamoto quotes, even in his last edition,[7] some incorrect values and misassignments for species of the discussed type has probably contributed, to some extent, to the delay of recognition of the correct relations between the ν_1 and ν_3 vibrations.

Finally, it should be remembered that similar rules which facilitate the assignment in the deformation region ($\nu_2(E)$ and $\nu_4(F_2)$ species) of tetraoxometalates are also well established.[8,9]

We hope that these brief comments will help solve definitively the assignment problems for these species.

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Convenient Procedure for the Conversion of Sodium Borohydride into Lithium Borohydride in Simple Ether Solvents

Sir:

Treatment of suspended sodium borohydride with lithium bormide in ethyl ether or tetrahydrofuran provides solutions of lithium borohydride readily separated from the precipitated sodium bromide. The heterogeneous metathesis is facilitated either by magnetic stirring or by mechanical stirring with glass beads present. This development makes lithium borohydride readily available from economical, readily available reagents.

In contrast to sodium borohydride, lithium borohydride is easily soluble in simple ether solvents such as ethyl ether and tetrahydrofuran.[1] Such solutions possess valuable reducing properties.[2] Unfortunately, commercial lithium borohydride is relatively expensive.[3] Moreover, there are problems in handling the solid.[4] There would be advantages to a procedure which would provide solutions of lithium borohydride in ethyl ether or tetrahydrofuran without the need for isolating or handling the solid.

Sodium borohydride is significantly soluble in isopropylamine,[5] ethanol,[6] isopropyl alcohol,[1] and diglyme,[1] and lithium borohydride has been prepared by metathesis with lithium chloride in all of these solvents[1,5,6] (eq 1). Unfortunately, it

$$NaBH_4 + LiCl \rightarrow LiBH_4 + NaCl\downarrow \qquad (1)$$

requires high temperatures to remove isopropylamine or diglyme from the lithium borohydride. More seriously, lithium borohydride undergoes fairly rapid hydrolysis in the alcohol solvents.[1] It appeared desirable to find a means of achieving the metathesis in EE or THF, solvents very commonly used for reductions.

No significant reaction was observed between sodium borohydride and lithium chloride vigorously stirred magnetically as suspensions in ethyl ether at 25 °C or reflux (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, lithium bromide and lithium iodide are soluble in ethyl ether.[7] Indeed, these reactions proved much more favorable, proceeding to essential completion in 48 h at 25 °C (eq 2). At reflux the reactions appeared to be essentially

$$NaBH_4 + LiBr \xrightarrow[48\ h]{25\ °C,\ EE} \underset{100\%}{LiBH_4 + NaBr\downarrow} \qquad (2)$$
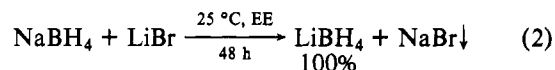
(1) El-Rafei, E. A. *Inorg. Chem.* **1981**, *20*, 222.
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(1) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1956**, *78*, 2582.
(2) Nystrom, R. F.; Chaikin, S. W.; Brown, W. G. *J. Am. Chem. Soc.* **1949**, *71*, 3245. Yoon, N. M.; Cha, J. S. *J. Korean Chem.* **1977**, *21*, 108.
(3) "Aldrich Catalog Handbook of Fine Chemicals", 1981–1982. "Alfa's Catalog of Research Chemicals and Materials", 1980–1981.
(4) For example, it has been reported that solid lithium borohydride has been known to flash on exposure to humid air (ref 2).
(5) Schlesinger, H. I.; Brown, H. C.; Hyde, E. K. *J. Am. Chem. Soc.* **1953**, *75*, 209.
(6) Kollonitsch, J.; Fuchs, O.; Gábor, V. *Nature (London)* **1954**, *173*, 126.
(7) Snover, J. H. Ph.D. Thesis, Purdue University Libraries, 1960.

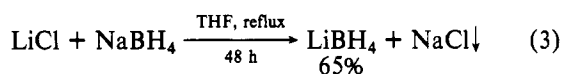**Table I.** Synthesis of Metal Borohydrides by Methathesis[a]

borohydride	salt	solvent	temp, °C	stirring[b]	% reaction					
					1 h	4 h	8 h	16 h	24 h	48 h
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[c]
NaBH$_4$	LiBr	EE	35	B	2		4		6	
NaBH$_4$	LiBr	EE	35	C	8	74[d]		98[e]		
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[f]	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[c]
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			
NaBH$_4$	CaCl$_2$	THF	25	A			38		88	
NaBH$_4$	CaCl$_2$	THF	67	C	26	92[h]	99			
NaBH$_4$	CaCl$_2$	THF	67	A	29	84	96			
NaBH$_4$	CaCl$_2$	THF	67	C	100					
KBH$_4$	LiCl	THF	25	A		100				
KBH$_4$	LiCl	THF	25	C	100[f]					

[a] 100 mmol of sodium or potassium borohydride stirred in 100 mL of ethyl ether (EE) or tetrahydrofuran (THF) with 1 equiv of salt.
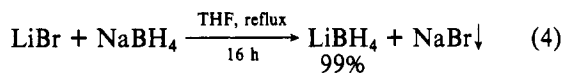[b] Stirring: A, magnetic stirrer; B, overhead mechanical stirrer; C, overhead mechanical stirrer with Teflon paddle and 25% by volume of 6-mm glass beads. [c] 32 h. [d] 6 h. [e] 12 h. [f] 2 h. [g] 10 h. [h] 5 h.

complete in 32 h. The bromide appeared to be slightly more favorable than the iodide. Consequently, we concentrated our efforts on the bromide.

Both lithium chloride and lithium bromide are soluble in tetrahydrofuran, and both salts reacted with sodium borohydride in that solvent. The reaction with lithium chloride proceeds to only 21% completion in 48 h at 25 °C and 65% completion in 48 h at reflux (67 °C) (eq 3). On the other

$$\text{LiCl} + \text{NaBH}_4 \xrightarrow[\substack{48\ h}]{\text{THF, reflux}} \underset{65\%}{\text{LiBH}_4} + \text{NaCl}\downarrow \quad (3)$$

hand, the reaction of lithium bromide went to 81% completion in 48 h at 25 °C and to 99% completion in 16 h at reflux (eq 4).

$$\text{LiBr} + \text{NaBH}_4 \xrightarrow[\substack{16\ h}]{\text{THF, reflux}} \underset{99\%}{\text{LiBH}_4} + \text{NaBr}\downarrow \quad (4)$$

It appeared that the problem had been solved, when we encountered an unexpected difficulty. These experiments had been carried out on a 100-mmol scale, using a magnetic stirrer. When Dr. Clinton F. Lane of Aldrich-Boranes, Inc., attempted to carry these reactions out on a larger scale, using mechanical stirring, the conversions decreased seriously. 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 magnetically stirred procedure. It appeared that the rapidly moving magnetic stirring bar must be producing an abrasion of the surface of the sodium borohydride 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, it actually improved the rate of reaction. In refluxing ethyl ether, the reaction of lithium bromide with sodium borohydride proceeded to 98% completion in 12 h (compare eq 2). In refluxing tetrahydrofuran, the reaction of lithium chloride with sodium borohydride

went to completion (100%) in 10 h (compare eq 3). Finally, under the same conditions, the corresponding reaction with lithium bromide was complete in 8 h (compare eq 4).

We experienced no difficulty in carrying out these preparations of lithium borohydride in ether solutions on an increased scale of 0.5 mol. Similarly, we experienced no difficulty in isolating solid lithium borohydride from these solutions.

We also tested the efficacy of this procedure for the Kollonitsch synthesis of calcium borohydride (eq 5).[8] Indeed,

$$\text{CaCl}_2 + 2\text{NaBH}_4 \xrightarrow{\text{THF, reflux}} \text{Ca(BH}_4)_2 + 2\text{NaCl}\downarrow \quad (5)$$
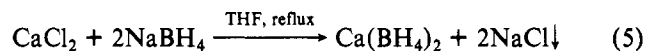
the reaction was complete in 1 h, as compared to the 4–8 h recommended in the original procedure.

We also established that the conversion of potassium borohydride into lithium borohydride in tetrahydrofuran at 25 °C is complete in 4 h with magnetic stirring and in 2 h with mechanical stirring with glass beads (eq 6).[9]

$$\text{KBH}_4 + \text{LiCl} \xrightarrow[\substack{2\ h}]{\text{THF, 25 °C}} \text{LiBH}_4 + \text{KCl}\downarrow \quad (6)$$
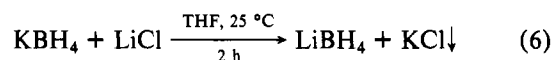
It should be pointed out that the use of ball mills to produce a grinding action on heterogeneous reaction mixtures is not new.[8,10] Possibly others have used glass beads with a paddle stirrer to facilitate heterogeneous reactions. However, in the present case, this device facilitates the synthesis in simple ether solvents of lithium borohydride from sodium borohydride, a transformation which had long escaped us.

The experimental results are summarized in Table I.
The following procedures are representative.

Stoichiometry of Reaction of Sodium Borohydride with Lithium Halide in Diethyl Ether Using Magnetic Stirring. In a typical experiment, a 250-mL round-bottom flask containing

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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 9.12 g (105 mmol) of lithium bromide. The flask was again flushed with nitrogen, and 100 mL of diethyl ether 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 under 25 °C with stirring for 48 h. White solid sodium bromide formed. The reaction mixture was then kept at 34 °C with stirring 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, collecting it 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] 275–278 °C dec). This was also confirmed by a ^{11}B NMR spectrum. The spectrum showed a quintet centered at −40.69 ppm in diethyl ether to the reference $BF_3 \cdot OEt_2$, identical with the behavior of commercial $LiBH_4$.

Stoichiometry of 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 sidearm containing glass beads (6-mm diameter, 180 g $\approx$ $^1/_4$ volume of the solvent), a mechanically operated Teflon paddle (9-cm 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, M. C. & B.) 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 were 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 conditions 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 using 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 0.53 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.

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Reformulation of the Molybdenum(I) Complex $[Mo(CNCMe_3)_4Cl]_2$ and Its Relevance to Previous Studies on Alkyl Isocyanide Complexes of Molybdenum and Tungsten

Sir:

Following the electrochemical oxidation of the homoleptic alkyl isocyanide complexes $[M(CNR)_7](PF_6)_2$ (M = Mo or W; R = CH_3, CMe_3, or C_6H_{11})[1,2] and the mixed alkyl isocyanide–phosphine complexes $[M(CNR)_6(PR'_3)](PF_6)_2$ (M = Mo or W; R = CH_3 or CMe_3; R' = Et, *n*-Pr, or *n*-Bu)[1,2] there is slow ligand loss (CNR in the case of $[M(CNR)_7]^{2+}$ and PR'_3 from $[M(CNR)_6(PR'_3)]^{2+}$) to produce ESR-active species, which we have suggested[1] might be the molybdenum(III) and tungsten(III) cations $[M(CNR)_6]^{3+}$. This possibility was given further credence when we became aware quite recently of the claim that $[Mo(CNCMe_3)_6](BF_4)_2$ can be prepared by the oxidation of $Mo(CNCMe_3)_6$ using silver tetrafluoroborate.[3] The synthetic route to $Mo(CNCMe_3)_6$ utilizes the potassium amalgam reduction of $[Mo(CNCMe_3)_4Cl]_2$,[5] a complex first described by King and Saran[4] back in 1974. Desirous of investigating the electrochemical properties of $[Mo(CNCMe_3)_6]^{2+}$, we set out to prepare this complex as its tetrafluoroborate salt. During the course of checking the recipe,[3] we found that our attempts to synthesize the complex purported to be $[Mo(CNCMe_3)_4Cl]_2$ led instead to the well-characterized molybdenum(II) complex $[Mo(CNCMe_3)_6Cl]Cl$.[6] The implications of this result are discussed in the present communication.

The yellow complex "$[Mo(CNCMe_3)_4Cl]_2$" is prepared[4] through the reaction of the (η^3-allyl)molybdenum(II) derivative (η^3-C_3H_5)Mo(CO)$_2$(NCCH$_3$)$_2$Cl with Me_3CNC in methylcyclohexane under reflux. We obtained a yellow product by the published procedure,[4] which, as far as we can tell, has properties that are fully in accord with those described in the literature.[7] Furthermore we find that the properties of this product are identical[8] with those of $[Mo(CNCMe_3)_6Cl]Cl$ as reported by Lippard and co-workers.[6] The conclusion that the latter formulation is indeed correct is further supported by microanalytical data. Anal. Calcd for $C_{30}H_{54}N_6MoCl_2$: C,

(1) Mialki, W. S.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 1380.
(2) Wood, T. E.; Deaton, J. C.; Corning, J.; Wild, R. E.; Walton, R. A. *Inorg. Chem.*, **1980**, *19*, 2614.
(3) Berry, D. E. Ph.D. Thesis, University of Bristol, 1977. We are grateful to Dr. Michael Green, University of Bristol, for drawing our attention to this work.
(4) King, R. B.; Saran, J. S. *Inorg. Chem.* **1974**, *13*, 2453.
(5) We have been informed by Professor G. Wilkinson, Imperial College, London, that an alternative route to $Mo(CNCMe_3)_6$ has been devised and that this will be the subject of a forthcoming paper.
(6) Lam, C. T.; Novotny, M.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1978**, *17*, 2127.
(7) We find the following properties for this product (literature data from ref 4 in parentheses): mp 162–164 °C dec (161 °C); $\nu(C\equiv N)$ (CH_2Cl_2 solution) 2137 s, 2117 sh cm^{-1} (2146 s, 2123 sh cm^{-1}); ^1H NMR δ 1.55, singlet (δ 1.57).
(8) In addition to the properties quoted in ref 7, we find that the electronic absorption spectrum of a methanol solution of this material has λ_{max} values of 400, 278, and 237 nm, in excellent agreement with literature data, viz., 404, 278, and 235 nm for an authentic sample of $[Mo(CNCMe_3)_6Cl]Cl$.[6]