Figure 1. ¹H nmr spectrum (60 MHz) of naphtho[b]cyclopropene in CCl₄.

low-field aromatic protons, double bond fixation (2a vs. 2b) may not be as extreme for this system as expected. In contrast, 1,2-diphenylnaphthocyclobutadiene (5) shows a high degree of double bond fixation and the central ring protons appear at δ 6.50, very close to the olefinic protons of cis-stilbene.[5] An X-ray structure determination of 2 is under way.
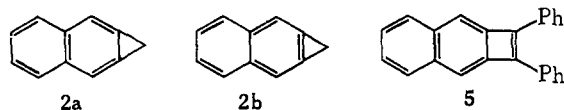
Hydrogenation of 2 over PtO₂ in ether at 25° gives benzocycloheptene (86%) and β-methylnaphthalene (14%). Naphtho[b]cyclopropene, like benzocyclopropene,[6] is sensitive to acid reagents. Thus, both 1 and 2 react slowly with acetic acid to give the corresponding benzylic acetates. The methanolysis of 2 is not detectable (nmr) after 4 hr at 25°; however, addition of 1 mol % Ag(I) to a 10% solution of 2 in methanol gives a quantitative yield of the ether 6 in <1 min at 25°, eq 2.
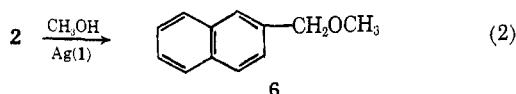

Attempts to find a base–solvent combination that gives a more rapid conversion of 3 → 2 than the KO-t-Bu–THF system have been largely unsuccessful. When KO-t-Bu in Me₂SO was used a low yield (<10%) of 2 was produced. The major products were 4 and β-vinylnaphthalene (7). The formation of 7 probably arises by reaction of 2 with potassium dimsyl to give 8. This compound would be expected to undergo elimination under the reaction conditions, eq 3.[7]

(5) M. P. Cava, B. Hwang, and J. P. van Meter, J. Amer. Chem. Soc., 85, 4032 (1963).
(6) Unpublished observations; see also S. Korte, Ph.D. Thesis, University of Köln, 1968.
(7) J. E. Hofmann, T. J. Wallace, P. A. Argabright, and A. Schriesheim, Chem. Ind. (London), 1243 (1963).

(3)
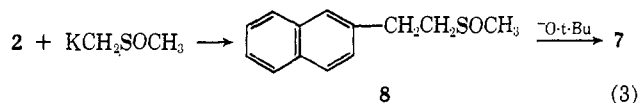
Finally, we can only speculate on the structure of the intermediates produced in the conversion 3 → 2. The sequence shown in eq 4 seems reasonable.

(4)
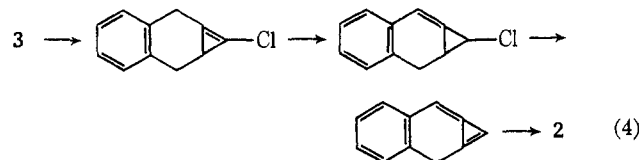
Acknowledgment. We gratefully acknowledge the Robert A. Welch Foundation for support of this work.

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The Rapid Quantitative Reaction of Potassium Hydride with Weak Lewis Acids. A Highly Convenient New Route to Hindered Complex Borohydrides[1,2]

Sir:

Potassium hydride reacts rapidly and quantitatively with weak Lewis acids such as hindered trialkylboranes, borate esters, and tetraalkyldiboranes. The reaction provides with unprecedented ease complex potassium borohydrides, certain of which have been demonstrated to be highly stereospecific reducing agents.

Potassium hydride (KH) is highly reactive toward metalation of weak organic acids such as dimethyl sulfoxide, amines, and hindered alcohols;[2] reactivity

(1) Kaliation. II.
(2) Part I: C. A. Brown, J. Amer. Chem. Soc., 95, 982 (1973).

markedly exceeds that of both NaH and LiH.[3] Both of the latter add to simple weak Lewis acids of boron in ether solvents.[4] However, increases in steric hindrance around boron greatly retard or completely preclude reaction.[4a,5] Examination of models reveals that approach of B in hindered trialkylboranes to the KH surface[6] is markedly more difficult than that of H–X in the Brønsted acids examined;[2] furthermore, formation of the borohydrides does not allow the possibility of a four-center reaction.
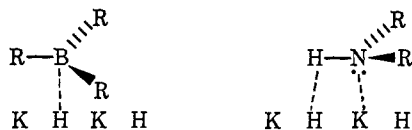
Reaction of KH suspended in tetrahydrofuran (THF) at 20–22° with pure tri-sec-butylborane proceeds rapidly with quantitative formation of potassium tri-sec-butylborohydride in less than 1 hr; in contrast NaH is very sluggish and LiH is inert, as shown in Figure 1.[7]

Similar rapid reaction is observed with tri-sec-butylborane prepared in situ by hydroboration of cis-2-butene with commercial borane–THF.[8] Other hindered organoboranes are readily "hydridokaliated," for example tricyclopentylborane, tricyclohexylborane, and tri-sec-pentylborane, as shown in Table I.

Table I. Reaction of Hindered Boron Lewis Acids with KH

Substrate[a]	KH, mmol	Temp, °C	Time, min	B–H yield, %[b]
Tri-sec-butylborane	35	20	60	100
Tri-sec-butylborane[c]	35	20	60	93
Tricyclopentylborane[c]	35	20	60	96
Tricyclohexylborane[c]	35	50	15	97
Tri-sec-pentylborane[c]	35	50	60	95
Triisopropyl borate[d]	51	20	30	104, 100
Tetra(3-methyl-2-butyl)-diborane[e,f]	35	20	15	65[e]

[a] 25.0 mmol; 0.95–1.00 M in THF. [b] Product solutions were analyzed by hydrolysis (±3% determination) in glycerin–water–HCl. Potassium (as base) agreed with active B–H. Products in THF exhibited consistent ir and [11]B nmr spectra. [c] Prepared in situ by hydroboration of appropriate alkene. [d] 0.65 M in THF. [e] Quantitative yield obtained on heating at 50° (see text). [f] 0.50 M in THF → 1.00 M borohydride.

The following procedure is representative. KH, 35 mmol (4.0 g of 35% dispersion in oil), was weighed under argon into a 100-ml round-bottomed flask (fitted with an injection port and TFE-covered magnetic stir bar). The flask was attached to a mercury

(3) LiH, NaH, and KH were produced and supplied by Alfa Products, a Division of Ventron Corp. For precautions in handling KH, see ref 2.

(4) (a) H. C. Brown, E. J. Mead, and C. J. Shoaf, J. Amer. Chem. Soc., 78, 3616 (1956); (b) H. C. Brown and W. C. Dickason, ibid., 92, 709 (1970), and references therein; (c) H. C. Brown and S. Krishnamurthy, ibid., 95, 1669 (1973).

(5) H. C. Brown and S. Krishnamurthy, J. Amer. Chem. Soc., 94, 7159 (1972).

(6) Potassium hydride is apparently completely insoluble in common ether solvents.

(7) (a) Even at reflux, LiH and tri-sec-butylborane react only 10% in 24 hr; see ref 5. (b) Similarly inertness is observed in the reaction of LiH with di-sec-butylmagnesium: E. C. Ashby and R. C. Arnott, J. Organometal. Chem., 21, 29 (1970).
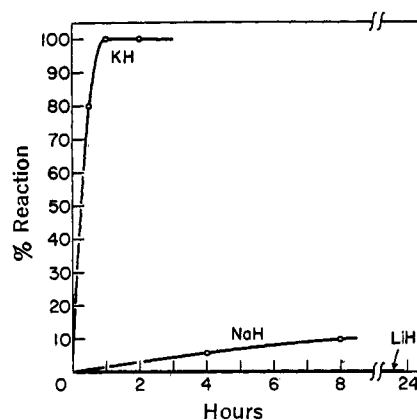
(8) Aldrich-Boranes, Inc.

Figure 1. Reaction of tri-sec-butylborane with saline hydrides in tetrahydrofuran at 20°.

bubbler and flushed briefly with argon or nitrogen and immersed in a 20° water bath. THF (dried by distillation from LiAlH₄ and stored under nitrogen) (15 ml) was added, followed by tri-sec-butylborane (6.0 ml, 25.0 mmol). After 1.0 hr the centrifuged solution showed that KH uptake had equalled the organoborane concentration and was constant. Ir of the solution showed a strong broad absorption at 4.95 μm (lit.[4b] for R₃BH⁻Li⁺ in THF, 4.95 μm). [11]B nmr exhibited a doublet (J = 71 Hz) centered 812 Hz upfield from external methyl borate. The downfield broad signal of tri-sec-butylborane was absent.

Triisopropyl borate in THF is nearly inert toward NaH at 20° and has been reported[4a] to require 83 hr at reflux to react with an excess of hydride. In contrast, KH reacts completely in less than 1 hr at 20°.

Tetra(3-methyl-2-butyl)diborane (I) reacts vigorously
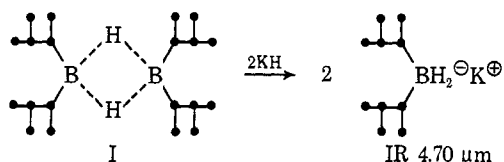
in THF at 20° to take up 0.6–0.7 KH per boron in 15 min. Further reaction is slow at 20° but is complete in 1 hr at 50°. NaH reacted only 5–8% in 18 hr at 20°.

Lithium tri-sec-butylborohydride (II) is highly stereoselective for reduction of cyclic ketones.[5] Potassium tri-sec-butylborohydride (III) appears to equal or

	% cis
II	99.3[5]
III	>99

	% cis
II	80.5[5]
III	88
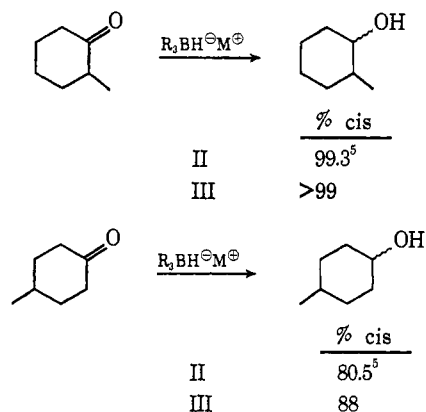
surpass the lithium compound, as shown by reduction of 2-methylcyclohexanone and 4-methylcyclohexanone.

It is apparent that KH is far more reactive toward hindered boron compounds than NaH or LiH. Reaction with KH provides a new route of unprecedented ease to highly hindered complex borohydrides; these reagents are of interest as specific reducing agents[9a] in synthesis and as tools for examining the effect of "B-strain" upon hydride transfer and reduction reactions. The materials also have potential for reduction of transition metal systems.[9b]

We are currently continuing investigations on reactions of KH and other saline hydrides with weak Brønsted and Lewis acids.

Acknowledgment. The author acknowledges financial assistance from the Research Corporation. Mr. Scott Hair aided with ^{11}B nmr; Dr. S. Krishnamurthy generously discussed unpublished data on the formation of trialkylborohydrides.

(9) (a) Potassium triisopropoxyborohydride appears to have unique properties as a reducing agent; it is currently under study. (b) Research in progress.

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Preparation of Ruthenium(0) and Osmium(0) Cyclooctatetraene Complexes

Sir:

Zerovalent complexes of metals in the iron triad continue to attract attention as potential catalysts,[1] as means of studying electrophilic and/or nucleophilic attack on coordinated organic molecules,[2] as models for "oxidative addition" reactions,[3] and, most recently, as desirable analogs to the known ML_5 complexes of d^8 configuration (*e.g.*, M = Rh(I), L = P(OMe)₃) found to be stereochemically rigid on the nmr time scale at low temperatures.[4] In general, however, synthetic routes to such species, particularly those not containing carbon monoxide,[5,6] have been severely limited. We wish to report here the preparation of some Ru(0) and Os(0) cyclooctatetraene complexes employing the dianion of cyclooctatetraene ([COT]$^{2-}$) as an efficient two-electron reducing agent. Preliminary studies show that the method may be used to prepare zerovalent complexes containing group Va ligands and that the Ru(0) cyclooctatetraene complexes will find application as catalysts and as preparative intermediates. This communication is concerned primarily with a description of the preparative method.[7]

Addition of a tetrahydrofuran solution of $[K^+]_2$-[COT]$^{2-}$ to a stirred suspension of [Ru(NBD)Cl₂]$_x$

(1) See, for example, A. Carbonaro, A. Greco, and G. Dall'asta, *J. Organometal. Chem.*, **20**, 177 (1969).

(2) See, for example, D. A. White, *Organometal. Chem. Rev., Sect. A*, **3**, 497 (1968).

(3) See, for example, J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, **87**, 4008 (1965); **88**, 3504 (1966).

(4) J. P. Jesson and P. Meakin, *J. Amer. Chem. Soc.*, **95**, 1344 (1973).

(5) The most successful method to date has been the isopropyl Grignard method developed by Fischer.[6] The application of this method toward preparation of complexes containing group Va ligands or the utility of the successfully synthesized complexes as preparative intermediates has yet to be demonstrated.

(6) J. Müller and E. O. Fischer, *J. Organometal. Chem.*, **5**, 275 (1966).

(7) All complexes reported in this communication have been fully characterized by elemental analyses and spectroscopic methods.

(NBD = bicyclo[2.2.1]hepta-2,5-diene) in THF yields a brown reaction mixture. Evaporation to dryness and extraction with pentane followed by chromatography on basic alumina (8% water, pentane eluent) yield (*inter alia*) orange plates of Ru(NBD)(COT) (**1**) in 20–30% yield by low-temperature crystallization. The infrared spectrum of **1** (Nujol) contains a band at 1670 cm^{-1} which is consistent with COT bonded as a tridentate ligand[8] while its temperature-dependent spectrum[9] is consistent with a five-coordinate ground-state geometry containing a plane of symmetry which bisects NBD (through the C=C bonds) and the tridentate COT ligand. The mass spectrum shows a parent peak at m/e 298.028 (calcd 298.029); significant loss of H_x (x = 1 or 2) from the parent ion is clearly indicated. The complex is very air sensitive in solution and mildly so in the solid state. Although it cannot be sublimed without decomposition, it may be stored indefinitely at $-30°$ under nitrogen.

Three other products have been isolated in lower yields. Two are found in addition to **1** under the above conditions, yellow Ru(NBD)(C₈H₁₀) (**2**, C_8H_{10} = 1,3,5-cyclooctatriene, 4% yield) and an intensely colored wine red dimeric species (**3**) whose precise composition is still uncertain.[10] Hydrogenation (or dehydrogenation) of unsaturated hydrocarbon ligands during preparation of complexes analogous to **1** has been observed by Fischer,[6] and formation of **2** is therefore not unexpected. Complex **3** is probably related to another dimeric species, Ru₂(NBD)₂(COT) (**4**), produced in low yield along with **2** and **3** upon stirring [Ru(NBD)Cl₂]$_x$, potassium metal, and cyclooctatetraene in THF. The nmr spectrum of **4**[11] is consistent with a structure in which COT bridges two metal–metal bonded Ru(NBD) moieties *via* 1,3-coordination to each.

The analogous reaction of [Ru(COD)Cl₂]$_x$ (COD = 1,5-cyclooctadiene) with [K$^+$]₂[COT]$^{2-}$ gave yellow crystals of Ru(COD)(C₈H₁₀)[12] and a yellow solid formulated as RuC₁₆H₂₀, both in 10% yield. A broad complicated nmr spectrum suggests that the latter is not solely Ru(COD)(COT); it is considered likely that COD has largely isomerized to what is formally a Ru(II) complex by formation of a π-allyl– and a σ-carbon–metal bond in a manner similar to that observed for Ru(COD)(CO)₃.[13] A trace (*ca.* 1%) of an orange species was isolated whose mass spectrum indicated it

(8) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 3444 (1966).

(9) The limiting spectrum was obtained at $-25°$ in toluene-d_8 at 100 MHz: τ 4.64 (2, dd, $J \approx$ 2 and 4 Hz, COT), 5.04 (4, m, COT), 5.86 (2, dd, $J \approx$ 2 and 8 Hz, COT), 6.88 (2, m, NBD methines), 7.28 (4, t, $J \approx$ 2, NBD olefins), 9.00 (2, t, $J \approx$ 1 Hz, NBD methylenes).

(10) The mass spectrum of **3** shows an apparent parent ion at m/e 490 although ready loss of H₂ from a species with m/e 492 cannot be ruled out at this time. The nmr spectrum of **3** in C₆D₆ at 220 MHz is exceedingly complicated, indicating the structure to be one of low symmetry.

(11) The nmr spectrum of **4** was recorded at 220 MHz in C₆D₆. Assignments were made with the aid of decoupling experiments. The COT resonances occur (in τ units) at -1.69 (2, dd, J = 1, 7 Hz), 2.84 (2, dd, J = 5, 7 Hz), 4.93 (2, ddd, J = 1, 5, 6.5 Hz), and 8.32 (2, d, J = 6.5 Hz). The NBD resonances occur at 6.48 (2, br s, NBD–CH), 6.80 (2, t, J = 3.5–4.0 Hz, NBD olefin), 6.92 (4, m, NBD olefin), 7.02 (2, br t, J = 3.5–4.0 Hz, NBD olefin), 7.58 (2, br s, NBD–CH), and 8.97 (4, br s, NBD–CH₂). The τ 8.97 peak is resolved into two broadened singlets ($\Delta\nu$ = 4 Hz) in CDCl₃ ($\Delta\nu$ = 1–2 Hz at 100 MHz in CDCl₃). A mirror plane of symmetry passing between the Ru nuclei is favored over a C_2 axis of symmetry.

(12) E. O. Fischer and J. Müller, *Chem. Ber.*, **96**, 3217 (1963).

(13) A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Organometal. Chem.*, in press.