phenolphosphine to yield the ylide complexes 3 and 4. A mechanism for enedionediolate formation involving the dimerization of species such as N, O suffers from two major deficiencies. First, the contributing hybrid N would appear, from the required distortion of the cumulene fragment, to be of prohibitively high energy content. Indeed, nitrogen lone-pair coordination to thorium is not observed in the isoelectronic ketenimine complexes 5-8 (vide supra).49 Thus, in this picture, carbone structure O would be the major contributor to a bonding description. However, we find that the reaction of 1 with CO to produce 2 is neither diverted by nor impeded by the addition of olefins. Thus, in the presence of ca. 3 equiv of trans-PhHC=CHPh or in neat Me2C-CMe2, no cyclopropane formation is observed and only complex 2 is detected as the reaction product. This result appears to argue against an intermediate such as O to account for the dimerization reaction.50

A second plausible pathway for the formation of 2 is shown in Scheme II. First, the rate-determining reaction of acyl 1 with CO to yield a transient ketene (step a) has already been discussed in ample detail. The second step b involves nucleophilic attack by CO on the ketene α-carbon to yield the new ketene complex 19. There is also ample support for this proposal. First, ylide complexes 3 and 4 are reasonably described as the nucleophilic interception products of such an intermediate (eq 6). Second, this type of coupling reaction directly parallels that proposed for the formation of 13 and 14 (Scheme I, step b). The reaction of isocyanides with keteniminium ions therefore provides a plausible model for the coupling of carbonyl monoxide with thorium-bound ketenes. The final step of this sequence involves a reaction of the ketene 19 with starting acyl 1 to form the observed product (2, step c).

(49) The substitution of the keteniminium nitrogen atom admittedly alters the tendency toward the formation of the ketene complex.
(50) It is difficult to predict the exact degree to which species such as O will conform to the behavior of typical heteroatom-substituted nucleophile carbenes (e.g., (MeO)2C). Sufficient nucleophilic character results in preferential dimerization over addition to olefins. However, monoycarbenes such as (PhO)(H)C: are readily trapped by simple olefins such as tetramethylethylene.15

In order to model this step of the sequence, the reaction between acyl 1 and diphenylketene was investigated. As described above, this reaction proceeds smoothly and quantitatively to form complex 15. This reaction can be understood formally in terms of an insertion of a ketene into a actinide-carbon bond to yield an alkoxide (eq 25).51 In the present example, the only difference is that a chelating alkoxide is formed. Therefore, justification


to form the observed product (2, step c).

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Registry No. 1, 99112-54-6; 2a, 99147-69-0; 2b, 99127-92-1; 2c, 99127-93-2; 3a, 99112-55-7; 3b, 99112-56-8; 4, 99112-57-9; 5, 99127-94-8; 6, 99112-60-0; 7, 99112-61-1; 8, 99112-58-0; 9, 99112-65-9; 10, 99112-59-1; 11, 99112-60-4; 12, 99112-61-5; 13, 99112-62-6; 14, 99112-63-7; 15, 99112-64-8; CuTh(CO)3(Ph); 99127-67-8; CuThCl(q2-COCH2Ph); 99147-68-9; PPh3, 603-35-0; PMe3, 594-09-2; r-BuNC, 7188-38-7; 2,6-Me2CH2NC, 2769-71-3; CH2=NC, 931-53-3; p-tolNC, 7175-47-5; CO, 630-08-0; COH, 1641-69-6; diphenylketene, 522-06-4.

Studies on the Mechanism of Transition-Metal-Assisted Sodium Borohydride and Lithium Aluminum Hydride Reductions

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Abstract: Studies on the course of transition-metal-assisted NaBH4 and LiAlH4 reductions of (1) nitrites, (2) alkenes, and (3) alkyl halides are described. (1) The kinetics of benzonitrile (PhCN) reduction indicate that at high nitrite catalyst ratios, the rate of reduction is independent of PhCN concentration. Furthermore, the rate of PhCN reduction exhibits a first-order dependence on NaBH4 concentration, as measured over a fourfold range of BH4- concentrations and several half-lives of PhCN. Moreover, when PhCN was reduced with equimolar mixtures of NaBH4 and NaBD4, a significant primary kinetic isotope effect was observed. Rapid complexation of PhCN to the boride surface apparently activates the nitrile group toward rate-determining hydride addition from dissolved, uncoordinated NaBH4. (2) The selective reduction of alkynes by NaBH4-CoCl2 is attributed to adventitious heterogeneous catalytic hydrogenation. (3) The combination of LiAlH4 with CoCl2 forms a black precipitate of cobalt aluminium (CoAl) which was isolated, analyzed by atomic absorption spectroscopy, and shown to play an essential catalytic role in the reduction of alkyl halides. Labeling experiments demonstrate stereochemical randomization by a heterogeneous process involving solvent as the hydrogen donor and LiAlH4 as a co-reductant. A radical mechanism involving halide atom transfer or oxidative addition to the aluminide is proposed.

Since their discovery four decades ago in the laboratories of Professor H. I. Schlesinger,1,2 both sodium borohydride (NaBH4) and lithium aluminum hydride (LiAlH4) have become the preeminent reducing agents of modern organic chemistry. All

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but the most refractory of functional groups can be reduced effectively with one or the other of these reagents in either protic or aprotic solvents. Moreover, ligand substitution at boron or aluminum, as well as counterion metathesis into other non-transition-metal hydrides, further broadens the scope and selectivity of such reductions. Work in this area is so extensive that the reader is directed to several current monographs and review articles for comprehensive summaries.

More recently, the use of transition-metal catalysts or co-reactants has added new dimensions to the versatility of NaBH₄ and LiAlH₄ reductions. Admixture of reagents like divalent cobalt, nickel, copper, palladium, and tin salts, or the corresponding rhodium(III), iridium(III), tin(IV), and titanium(IV) halides, creates systems which are capable of reducing alkenes, alkyl and aryl halides, alkynes, amides, amines, azides, carboxylic acids and acid chlorides, esters, indoles, lactams, lactones, nitriles, nitro, and nitroso compounds. Even this subset of boron and aluminum hydride literature is too voluminous to summarize here; fortunately, an excellent and timely review article appeared in 1983.

Virtually nothing is known about the detailed mechanisms of these "transition-metal-assisted" hydride reductions. For instance, it is often unclear whether the metal halide co-reactant serves a true catalytic function or whether some transient, low-valent transition-metal (hydride?) complex formed in situ is the actual reducing agent in these heterogeneous hydride reduction catalysts. It may be implicated, functioning with hydrogen provided by the decomposition of NaBH₄ or LiAlH₄. In some cases, insoluble transition-metal borides appear which can act as heterogeneous hydrogenation catalysts. It is an unfortunate fact that many publications in this area neglect to report crucial experimental details about precipitate formation or gas evolution which might shed light on questions of mechanism.

This manuscript describes studies on the course of transition-metal-assisted NaBH₄ and LiAlH₄ reductions of (1) nitriles, (2) alkenes, and (3) alkyl halides. Our investigation focused on Co(II)-mediated reductions since the literature on these is so extensive. By isolating and examining the individual components of heterogeneous reaction mixtures, we have unambiguously identified borides and aluminides of cobalt as catalysts in all three reductions. Some of our findings are quite surprising and clearly at odds with commonly held notions about the mechanisms of these processes.

Results and Discussion

Nitrile Reductions Using Cobalt Boride. In 1980, we used NaBH₄ in combination with CoCl₂ to reduce a nitrile to its corresponding primary amine at room temperature in CH₃OH. A black precipitate containing >95% of the cobalt (as Co₂B) was formed. This method should prove valuable in selective synthetic processes.

Although early experiments indicated that nitriles were adsorbed on the boride surface prior to reduction, they could not distinguish whether free NaBH₄ or some other, more complex reducing agent coordinated to the boride was the actual "hydride" donor. Likely candidates, to name a few, would be multinuclear, bridged borohydridocarbene complexes. We examined Co₂B, although stoichiometric quantities of the boride appeared necessary. Reasons for this were unclear at the time of our communication, since "spent" boride from TAB nitrile reductions actively catalyzed reduction of nitriles by NaBH₄. To address this question we examined the solvent and pH dependence of reduction as well as the mode of boride preparation.

The pH of the reaction medium proved to be the key. Whereas mixtures of NaBH₄ and Co₂B in CH₃OH became basic (pH 8.5-9.0) during borohydride decomposition, solutions of TAB in CH₃OH with Co₂B proved stable, evolving negligible quantities of H₂ and remaining neutral. When the pH of TAB-CH₃OH solutions was brought to ca. 8-9 with NaOCH₃ (no H₂ evolution), the reduction of benzonitrile to benzylamine (91% yield), indicating the effect of solvent on boride formation. In both cases, the pH upon completion of reduction was the same (ca. 10.0). Other experiments with Co₂B freshly prepared each time in situ confirmed that reductions in aqueous solution were more rapid than reductions in methanol. An optimized procedure for the reduction of nitriles has now been developed which uses catalytic quantities of Co₂B in 2:1 THF:H₂O and avoids the harshly acidic workup of past procedures.

Besides sodium borohydride, certain amine boranes like tert-butyliamine-borane (TAB) could be used to reduce nitriles in CH₃OH in the presence of Co₂B, although stoichiometric quantities of the boride appeared necessary. For this reason we were unclear at the time of our communication, since "spent" boride from TAB nitrile reductions actively catalyzed reduction of nitriles by NaBH₄. To address this question we examined the solvent and pH dependence of reduction as well as the mode of boride preparation.

In our preliminary communication about the mechanism of this reaction, we concluded that the cobalt boride formed in situ served as a true catalyst, strongly coordinating nitriles and activating them toward reduction by NaBH₄. Since sodium borohydride reacted with CH₃OH at a rapid rate and metal borides further accelerated this breakdown, a large excess NaBH₄ was required to consume all the reactant.

Because NaBH₄ is considerably more stable in water than in methanol, the use of aqueous solvents was explored. When a solution of benzonitrile in 2:1 THF:H₂O was treated with excess NaBH₄ and Co₂B (0.1 mol-equiv prepared in CH₃OH), only small quantities of benzylamine were produced. Substituting a comparable amount of CoCl₂ for Co₂B in the same experiment efficiently furnished benzylamine (91% yield), indicating the effect of solvent on boride formation. In both cases, the pH upon completion of reduction was the same (ca. 10.0). Other experiments with Co₂B freshly prepared each time in situ confirmed that reductions in aqueous solution were more rapid than reductions in methanol. An optimized procedure for the reduction of nitriles has now been developed which uses catalytic quantities of Co₂B in 2:1 THF:H₂O and avoids the harshly acidic workup of past procedures.


half-life of benzonitrile under various reduction conditions rather than attempt to determine rate constants with a high degree of precision. Our findings can be summarized as follows.

(1) At nitrite-catalyst ratios of 10–20, the rate of reduction was observed to be independent of benzonitrile concentration. This finding is consistent with the rapid, reversible coordination of nitrite to catalyst as a prerequisite for reduction.

(2) The rate of benzonitrile reduction exhibited a first-order dependence on NaBH₄ concentration, as measured over a fourfold range of NaBH₄ concentrations and several half-lives of PhCN.

(3) When benzonitrile was reduced with equimolar mixtures of NaBH₄ and NaBD₄, the product was shown by mass spectrometry to contain 58.5% d₆, 35.2% d₅, and 6.3% d₄ benzonitrile. Assuming that both hydride addition steps leading to amine are subject to comparable isotope effects, the data are consistent with a kᵦ/kₒ of 3.3 (±0.5).

Several mechanistic conclusions can be drawn from these findings. (1) Simple complexation or bridging of borohydride to the catalyst surface can be ruled out as the rate-determining step, since adsorption must be accompanied by substantial B–H bond-breaking in order to explain the pronounced primary kinetic isotope effect. (2) Rate-determining, boride-induced decomposition of NaBH₄ might form some "cobalt hydride" along with transient, surface-bound BH₃ functioning as the actual reducing agent. Although such a step would be consistent with our kinetic observations, we could find no direct evidence that free or coordinated boronate was involved. We have shown that cobalt boride does indeed alter the normal mode of BH₃ decomposition in water or alcohol. However, since nitride reductions maintain a first-order dependence on borohydride even at high BH₃⁺ concentrations, a rate-determining decomposition of NaBH₄ would require an extremely weak affinity of BH₃⁺ for the boride and an unusually large rate constant for the hydride transfer step, both of which seem unlikely. (3) The most straightforward mechanism consistent with our findings is that complexation of benzonitrile to the boride surface activates the C=N group toward rate-determining hydride addition from dissolved, uncoordinated NaBH₄ as pictured below.

Alkene Reductions Using Cobalt Boride. Many transition-metal salts promote the reduction of alkynes and alkenes by NaBH₄. Recently two reports on cobalt-based systems appeared. In 1979 Chung reported that alcoholic NaBH₄-CoCl₂ could selectively reduce alkynes as well as mono- and disubstituted alkenes in the presence of more highly substituted olefins. The selective monohydrogenation of limonene was described. No mechanism was proposed, but a cobalt hydride species was invoked as the active reducing agent. In 1984 Satyanarayana and Periasamy reported the solvent dependency of this reduction and contended that reaction of NaBH₄ with CoCl₂ produced either "Co₃H₇" (in THF–CH₂OH) or "BH₃" (in THF). Selective hydrogenation of mono- and disubstituted alkenes in CH₂OH was ascribed to the former species while reductions in THF produced nonvolatile residues (uncharacterized, but presumed to be trialkylboranes) which could subsequently be oxidized to alkanoic acids with H₂O₂–NaOH. Because of some contradictions with our own work and because important control experiments were not mentioned, we decided to investigate these findings in greater detail.

First we demonstrated that selective hydrogenations reported by Chung with ethanolic CoCl₂-NaBH₄ could equally well be achieved under heterogeneous conditions with preformed Co₂B and H₂ gas. The boride alone (1 equiv) was incapable of reducing limonene. Homogeneous hydrocobaltation may be considered unlikely since CoCl₂ formed Co₂B so rapidly that "Co₃H₇" species would be fleeting intermediates at best. Nucleophilic attack by NaBH₄ on a homogenous alkene–cobalt complex also seemed improbable for the same reasons. While it is conceivable that NaBH₄ might attack a heterogeneous alkene–Co₂B complex, the fact that limonene could not be reduced over Co₂B with NaBH₄ or LiBH₄ in either THF or 12% THF-CH₂OH (where H₂O₂ is suppressed) rendered this a remote possibility. Heterogeneous hydrogenations over both cobalt and nickel boride are, in fact, well-precedented. In the Chung system it would appear that NaBH₄ is functioning as a source of H₂ via decomposition over Co₂B.

We also reinvestigated the combination of undissolved NaBH₄ (2 mol-equiv) with solid CoCl₂ suspended in anhydrous THF, which was reported to generate BH₃⁺. In fact this proved to be a complex heterogeneous reaction (3 solid phases) in which a fine black precipitate (presumably cobalt boride) slowly formed while the supernatant retained its characteristic blue color [Co(II)] even after prolonged stirring. Controls showed that if BH₃⁺ were generated, it would have reacted with dissolved CoCl₂ to form more boride. Transient BH₃⁺ could not be trapped with 1,5-cyclooctadiene (COD) to form 9-borabicyclo[3.3.1]nonane (9-BBN) because a control showed that even 9-BBN was unstable to the reaction conditions. Nevertheless, adding COD (1 mol-equiv) to the system did form a complicated nonvolatile product mixture whose NMR spectrum closely matched that of the 9-BBN control experiment. Thus it is possible that BH₃⁺ and other substituted boranes may be fleeting intermediates, but the indirect evidence so far obtained pertains only to reactions run under these highly heterogeneous, aprotic conditions.

Alkyl Halide Reductions Using Cobalt Aluminide. Combinations of LiAlH₄ with Co(II), Ni(II), Fe(II), Fe(III), Ti(III), V(III), and Cr(III) halides have been studied extensively by Ashby et al. as reducing agents for alkynes, alkenes, and alkyl halides in tetrahydrofuran solution. Of these, only the CoCl₂-, NiCl₂-, and TiCl₃-based systems were active with catalytic quantities of the transition-metal salt. Little is known about the actual mechanism of these transformations, although they have commonly been grouped together as a class of "transition-metal hydride reductions". Since black precipitates were reported to form, we decided to investigate their involvement in the reduction of alkyl halides.

In 1956, Stewart and Schaeffer described the reduction of cobalt(II) bromide with LiBH₄ and LiAlH₄ in diethyl ether. Excess LiAlH₄ reacted with CoBr₂ to give 4 mol-equiv of hydrogen and a black, pyrophoric precipitate which contained all the aluminum. The precipitate, designated "cobalt aluminide" (CoAl₂), reacted with methanol to form trimethoxyaluminum and a new...
black suspension of finely divided cobalt, as given in the equations below.

\[
\begin{align*}
\text{CoBr}_2 + 2\text{LiAlH}_4 &\rightarrow \text{CoAl}_2 + 2\text{LiBr} + 4\text{H}_2 \\
\text{CoAl}_2 + 6\text{CH}_3\text{OH} &\rightarrow (2\text{CH}_3\text{O})_2\text{Al} + \text{Co} + 3\text{H}_2 \\
\text{Co} + 2\text{H}^+ &\rightarrow \text{Co}^{2+} + \text{H}_2
\end{align*}
\]

This synthesis of cobalt aluminide was reproduced exactly as described, and by analyzing the precipitate with argon plasma emission spectroscopy an empirical formula of CoAl\(_{1.1}\) was obtained. Although this composition varied slightly with the reaction solvent (THF or ether), the particular cobalt halide salt used, and even the manner and rate of mixing, a minimum of 1.5 mol-equiv of \(\text{LiAlH}_4\) was always required for complete CoCl\(_2\) reduction. Adding solid CoBr\(_2\) to diethyl ether solutions of LiAlH\(_4\) consistently gave precipitates with the highest average aluminum content. Combining homogeneous THF solutions of CoCl\(_2\) and LiAlH\(_4\) resulted in very finely divided cobalt aluminide possessing the lowest aluminum content (CoAl\(_{1.5}\)). Despite difficulties in filtering or centrifuging such finely divided aluminide, the latter procedure was the most reproducible and was therefore adopted for mechanistic studies on alkyl halide reduction.

The reduction of bromocyclohexane was chosen as a representative case since LiAlH\(_4\) alone (1 mol-equiv, THF, reflux, 24 h) produced cyclohexene in 12% yield along with starting material (71%). In the presence of CoCl\(_2\) (0.1 equiv), hydrogen was evolved and cyclohexene (64%) was bromocyclohexane (26%) were detected after the same reaction period. To define the role of the cobalt, mixtures of LiAlH\(_4\) and CoCl\(_2\) were partitioned by centrifuging the black precipitate and decanting the supernatant under argon. The residual aluminide was rinsed with solvent to remove any THF-soluble metal hydrides.

Controls established that fresh supernatant prepared in this fashion contained only residual LiAlH\(_4\) and no new soluble reducing agent. When washed cobalt aluminide (10 mol %) was suspended with bromocyclohexane in fresh THF, cyclohexene (ca. 20%) was formed very sluggishly. However, if LiAlH\(_4\) was added to the mixture of cobalt aluminide and bromocyclohexane, the yield of cyclohexene rose to 85% after 24 h. These experiments strongly suggested that cobalt aluminide acting as a catalyst was primarily (if not exclusively) responsible for promoting the reduction of alkyl halides by LiAlH\(_4\).

The lithium borohydride reduction of alkyl halides was likewise promoted by cobalt aluminide. For example, 1-chlorodecane, normally inert to LiBH\(_4\) in THF at 65 °C, formed decane (52%; 32% recovered SM) when the aluminide was added.

To determine the stereochemistry of cobalt aluminide mediated alkyl halide reductions, pure samples of both cis- and trans-4-bromo-tert-butylcyclohexane (1 and 2, respectively)\(^{22}\) were exposed to LiAlD\(_4\), in THF, with and without CoCl\(_2\). Products were analyzed by gas chromatography (GC), deuterium NMR, and mass spectrometry (MS). For reference, authentic samples of cis- and trans-4-tert-butylcyclohexane-1-d\(_5\) (3 and 4) were prepared as described by Wiseman, who has also reported their \(^1\)H NMR spectra.\(^{23}\) The results of this investigation are summarized in Table 1.

Control reductions with LiAlD\(_4\) alone (48 h, 65 °C) gave as anticipated a mixture of starting material and tert-butylcyclohexane. Elimination of axial bromide 1 additionally afforded small amounts of 4-tert-butylcyclohexene (5), which was not further reduced to any appreciable extent. In both controls, 9:1 ratios of \(d_4:d_0\) cycloalkanes were detected by mass spectrometry, corresponding closely to the deuterium content of the reducing agent. Moreover, \(^1\)H NMR indicated complete hydrogenation had occurred. Traces of 4-deuterio-1-butanol (resulting from competing reduction of THF) were also detected by GC, MS, and \(^1\)H NMR.

Reduction of 1 and 2 by LiAlD\(_4\) in the presence of CoCl\(_2\) (0.1 equiv) gave unexpectedly different results. The product tert-butylocyclohexane from both 1 and 2 was 83–84% undeuterated and ca. 16% monodeuterated at C4. In each case \(^1\)H NMR indicated the minor product had formed by reduction with predominant inversion of configuration, as would be expected from the competing, uncatalyzed reduction pathway. The preponderance of undeuterated product suggested that the CoAl-mediated reduction involved H-atom abstraction from solvent (THF) and not from the hydride source. In fact, GC–MS analysis of the volatile products from such reduction mixture confirmed the presence of a solvent dimer, most likely 6.

Two plausible mechanisms (see Scheme I) for a radical-type reduction pathway are (i) halogen atom transfer from the alkyl halide to a metal radical on the aluminide surface\(^{24}\) or (ii) oxidative addition of the cobalt atom into the carbon–halogen bond. The latter process would generate a labile alkylcobalt species whose homolytic cleavage is well-precedented in the chemistry of vitamin B\(_12\) and its analogues.\(^{25}\) Either mechanism, if correct, would indicate a secondary role for LiAlH\(_4\), serving not to reduce the alkyl halide but to regenerate the active (presumably reduced) form of the aluminide catalyst.\(^{26}\) To test this hypothesis and to establish the key role of solvent in determining the overall stereochemistry of reduction, deuterium-labeled bromide 7 was prepared from the corresponding ketone. When 7 was exposed to a stoichiometric quantity of freshly prepared, thoroughly washed cobalt aluminide in THF in the absence of added LiAlH\(_4\), the

---

Table I

<table>
<thead>
<tr>
<th>halide</th>
<th>reagents(^{22})</th>
<th>recovered SM</th>
<th>yield of tert-butylcyclohexane (^{[3]: unlabeled})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LiAlD(_4)/THF</td>
<td>37%</td>
<td>7%</td>
</tr>
<tr>
<td>2</td>
<td>LiAlD(_4)/CoCl(_2)/THF</td>
<td>4.7%</td>
<td>2.6%</td>
</tr>
<tr>
<td>3</td>
<td>LiAlD(_4)/THF</td>
<td>57%</td>
<td>93%</td>
</tr>
<tr>
<td>4</td>
<td>LiAlD(_4)/CoCl(_2)/THF</td>
<td>15%</td>
<td>4%</td>
</tr>
</tbody>
</table>

\(\text{LiAlD}_4 + \text{CoCl}_2 + \text{THF} \rightarrow \text{CoAl}_2 + 4\text{H}_2 + \text{LiBr} + 2\text{LiAlD}_4\)

\(^{22}\) All reactions were conducted for 48 h at 65 °C in THF under Ar. \(^{23}\) In runs containing CoCl\(_2\), 0.1 mol-equiv was used.
halide was reduced to a 43:57 mixture of 3 and 4. This unambiguously experiment is only consistent with a heterogenous, radical pathway for the reduction of alkyl halides by LiAlH₄–CoCl₂. The reduction of haloalkanes with LiBH₄–CoAl probably involves a similar mechanism.

**Conclusion**

Many transition metals catalyze the reduction of functional groups which are inert to NaBH₄ or LiAlH₄ alone. Moreover, several large-scale commercial processes rely on hydride-reduced transition-metal catalysts. These systems vary widely in their compositions, stoichiometry, and probably also the mechanisms by which they operate. The work reported here, though limited per se to cobalt-catalyzed reactions, may also be relevant to reducing agents in which hydride reagents are combined with Mn, Fe, Ni, Cu, Ru, Rh, Pd, Os, Ir, and Pt salts—all of which could form borides or aluminides. A better mechanistic understanding of those processes should greatly extend the scope and utility of borohydride and aluminium hydride mediated transformations.

**Experimental Section**

General. Reagent grade methanol and absolute ethanol were used without further purification. Tetrahydrofuran (THF) was distilled from sodium benzenophene prior to use. Benzotriazole and all alkyl halides were also distilled prior to use. Anhydrous CoCl₂, lithium borohydride, sodium borohydride, and lithium aluminium hydride were obtained from Alfa-Aesar. Cobalt chloride hexahydrate was obtained from Fisher Chemical Co. For Co₆Al₁₆ reactions, stock solutions of LiAlH₄ were prepared by diluting a commercial solution with dry THF and storing them in flasks protected from the air. These solutions were titrated according to the method of Villarreal. Thirty stock solutions (saturated with ν = 0.025 M of anhydride, ν = 0.15 M dry THF) were prepared and stored in similar fashion. All reactions were conducted under Ar or N₂ unless otherwise noted. A Sage Model 341 motor drive was used as a syringe pump. Proton NMR spectra of CdCl₂ solutions were recorded on a Bruker WM-300 or Varian XL-200 spectrometer at room temperature. Proton NMR experiments were also performed on the Bruker WM-300, with integrations measured five times for precision. Chemical shifts in ppm were measured relative to internal tetramethylsilane. Relaxation shifts in ppm were measured relative to internal tetrarmethylsilane. Transmission (T) experiments were run to determine adequate delays for accurate integrations. Gas-liquid chromatography of benzonitrile, bromocyclohexane, and 1-chlorocyclohexene was performed on a Hewlett-Packard (H-P) 5750 instrument equipped with a Spectro-Physics Minigrator. Analyses of benzotriazole were carried out on a 6 ft 10% Pennwalt 223-4% KOH column at 120 °C. Alkyl halides were analyzed on a 6-ft SE-30 column. Calibration curves were generated for each substrate with n-decane as an internal standard for benzotriazole and n-dodecane for 1-chlorocyclohexane and bromocyclohexane. GLC response factors for reactants and products were determined to ensure accurate yield calculations. Routine analyses of benzonitrile were carried out on a 6 ft 10% Pennwalt 223-4% KOH column at 120 °C. Alkyl halides were analyzed on a 6-ft SE-30 column. Calibration curves were generated for each substrate with n-decane as an internal standard for benzotriazole and n-dodecane for 1-chlorocyclohexane and bromocyclohexane. GLC response factors for reactants and products were determined to ensure accurate yield calculations.

**Optimum Reduction of Nitriles Using NaBH₄ and CoCl₂ in 2:1 THF/H₂O.** The following is a representative procedure. A stock solution of CoCl₂-6H₂O (0.445 g, 1.87 mmol) and benzotriazole (1.92 g, 18.6 mmol) in THF (66 mL, distilled) and water (33 mL) was stirred vigorously and cooled intermittently with an ice-water bath while NaBH₄ (1.40 g, 37.1 mmol) was added in portions over 8 min. The reaction was exothermic, producing a black precipitate and copious quantities of hydrogen. TLC analysis after 50 min indicated traces of starting material, so additional NaBH₄ (0.41 g) was added. After a total time of 2 h, 28% NH₄OH solution (2 mL) was added and the mixture transferred to centrifuge tubes. After 15 min, the supernatant (two liquid phases) was decanted and the sediment washed with more of the same solvent. The combined supernatants were concentrated under reduced pressure to remove the bulk of THF, then the aqueous residue was extracted with 4 × 40 mL of CH₂Cl₂. The combined CH₂Cl₂ layers were dried (MgSO₄) and concentrated to afford benzylamine (1.82 g, 91%) as a pale oil, identical in every respect with an authentic sample.

**Kinetics of Benzonitrile Reduction.** To a 100-mL round-bottomed one-necked flask equipped with T/H, 1/10 in. magnetic stirbar was added a solution of CoCl₂-6H₂O (0.179 g, 0.75 mmol) in ethanol (35 mL). After the sample was equilibrated in a 210 °C water bath, a solution of NaBH₄ (0.064 g in 5 mL of ethanol) was added to the vigorously stirred solution by syringe pump over 1.5–2 min. Gas evolution was observed as the black precipitate of Co₂B formed. After 15 min, a solution of benzotriazole (0.775 g, 7.5 mmol in 15 mL of ethanol) was added. The flask and contents were equilibrated for 15 min, then finely pulverized NaBH₄ (0.567 g, 15.0 mmol) was added to the solution. One-milliliter aliquots of the heterogeneous reaction mixture were withdrawn by syringe every 15 min and injected into dilute HCl (2 mL of 1.9 concentrated HCl/H₂O). Each aliquot was shaken vigorously to decompose both NaBH₄ and Co₂B and then centrifuged and the supernatant was analyzed by GLC.

Each run was performed in duplicate and monitored for 2 h. Concentrations of both NaBH₄ and benzotriazole were varied as shown below. In the run where the benzotriazole concentration was doubled as was doubled with control. Control experiments in which no solid NaBH₄ was added to mixtures of PhCN and Co₂B showed that less than 1% reduction had occurred after 2 h. Results ([NaBH₄], [PhCN], T₁/₂ (T₂ is the time required for one-half the benzotriazole to be consumed)) are as follows:

<table>
<thead>
<tr>
<th>Run</th>
<th>[NaBH₄]</th>
<th>[PhCN]</th>
<th>T₁/₂</th>
<th>T₁/₂ (for PHCN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.30 M</td>
<td>0.15 M</td>
<td>1700 ± 250 s</td>
<td>900 ± 150 s</td>
</tr>
<tr>
<td>2</td>
<td>0.60 M</td>
<td>0.15 M</td>
<td>950 ± 150 s</td>
<td>450 ± 150 s</td>
</tr>
<tr>
<td>3</td>
<td>0.30 M</td>
<td>0.30 M</td>
<td>3150 ± 350 s</td>
<td>1575 ± 150 s</td>
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**Competitive Reductions with NaBH₄/NaBD₄. Run 1.** To a rapidly stirred solution of CoCl₂-6H₂O (0.179 g, 0.75 mmol) in absolute ethanol (35 mL) was added a fresh solution of NaBH₄ (0.064 g, 1.70 mmol in EtOH (5 mL) over 130 s by syringe pump. The reaction flask was kept at 23 °C in a water bath. After 15 min an intimate mixture of (0.066 g, 14.6 mmol) and NaBD₄ (0.608 g, 14.6 mmol) was added followed by a solution of PhCN (0.100 g, 0.97 mmol) in EtOH (0.65 mL). The mixture was stirred for 75 min, and then 25 mL of 10% aqueous HCl was added to terminate reduction. The solvent was removed in vacuo and the residue dissolved in 15 mL of 0.082 g (78%) of a pale yellow oil. Run 2. The above procedure was repeated exactly as described but with use of a larger excess of NaBH₄ (0.734 g, 19.4 mmol) and NaBD₄ (0.821 g, 19.4 mmol).

**Selective Alkenes Reduction Using Co₃B–H₂.** To a 25-mL round-bottomed flask equipped with stirbar was added freshly made Co₂B (0.514 g, 4 mmol, limonene (Aldrich Chemical Co. 0.648 mL, 4 mmol), and absolute EtOH (12 mL). The system was flushed and maintained under an atmosphere of H₂ for 12 h. The reaction mixture was acidified (3 N HCl, 10 mL) to decompose the boride and the product extracted with 15 mL of ether. The solvent was removed by syringe pump over 130 s by syringe pump. The reaction flask was kept at 23 °C in a water bath. After 15 min an intimate mixture of (0.066 g, 14.6 mmol) and NaBD₄ (0.608 g, 14.6 mmol) was added followed by a solution of PhCN (0.100 g, 0.97 mmol) in EtOH (0.65 mL). The mixture was stirred for 75 min, and then 25 mL of 10% aqueous HCl was added to terminate reduction. The solvent was removed in vacuo and the residue dissolved in 15 mL of 0.082 g (78%) of a pale yellow oil.

**Analysis of Co₃B.** To an oven-dried 50-mL round-bottomed centrifuge tube equipped with a T/H, 1/10 in. magnetic stirbar was added a solution of anhydrous CoCl₂ in THF (30 mL of a 0.024 M solution, 0.73 mmol). The flask was cooled to −40 °C in a dry ice-acetone bath, and then dissolved LiAlH₄ (1.6 mL of a 0.45 M solution, 0.73 mmol) was added over 1 min with stirring. The solution was then dried over MgSO₄ and filtered. Concentration in vacuo afforded 4-isopropyl-1-methyl-1-cyclohexene in 95% yield along with 15% of recovered limonene.

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Partitioning the LiAlH₄/CoCl₂ Reagent for Reduction of Bromocyclohexane. To an oven-dried 10-mL Kimble vial equipped with rubber septum and stirbar was added a solution of anhydrous CoCl₂ (0.05 mmol in 2 mL of THF). Lithium aluminum hydride (0.074 mmol in 0.5 mL of THF) was added without stirring and a black deposit of CoAl₂ appeared instantly. After 30 min the vial was centrifuged and the brown supernatant transferred to a fresh dry vial. The supernatant deposited more brown precipitate upon standing, so it was centrifuged again and the nearly colorless THF solution decanted into another vial. Meanwhile the original Kimble vial containing CoAl₂ was washed with dry THF (2 mL).

To the tubes containing clear supernatant and washed aluminate was added a solution of bromocyclohexane (0.081 g, 0.50 mmol) and dodecane (0.050 g) in dry THF (1 mL), followed by 1.2 mL of a 0.35 M solution of LiAlH₄. Each tube was brought to a final volume of 5 mL with THF, stoppered, and heated to 65 °C for 24 h. After the solution was cooled, water (5 drops) was added to each reaction, the vials centrifuged, and the supernatants analyzed by GLC.

When the aluminate prepared exactly as above was heated alone with bromocyclohexane (24 h, 65 °C in THF, no LiAlH₄ added), GLC analysis revealed 21% cyclohexane and 79% bromocyclohexane.

Reduction of 1-Chlorodecane with CoAI₂ and LiAlH₄. An oven-dried 10-mL Kimble vial fitted with septum and stirbar containing CoCl₂ (0.017 g, 0.13 mmol) in THF (5 mL) was treated with LiAlH₄ (1.40 g, 0.14 M solution in THF) and a stock solution of bromocyclohexane (0.109 g, 0.50 mmol) in THF (0.12 mL). Gas was evolved and a black precipitate was washed twice with dry THF (1.5 mL) and then treated with (MgSO₄), filtered, and concentrated to afford a colorless oil (42 mg, 22%). When the oil was dissolved in acetone, triphenylphosphine oxide precipitated and was filtered. The combined acetone filtrate and hexane extracts were concentrated and the residue chromatographed on a silica gel column (40 mm × 10 cm). Several mixed fractions of bromide contaminated with alkene were obtained. These were eluted with hexanes, and a stream of ozone passed through the solution until TLC indicated complete consumption of 5.

The reaction mixture was cooled to room temperature and treated with CoCl₂·H₂SO₄ (Jones reagent, 0.5 mL) then with 3-propanol (3 mL), and the resulting orange mixture was filtered, and the filtrate was washed with water. The aqueous phase was extracted with THF, and the combined organic extracts were washed with dry THF, stoppered, and heated to 65 °C for 24 h. After the solution became homogeneous, the reaction mixture was filtered through the solution until TLC indicated complete consumption of 5. The reaction mixture was warmed to room temperature and treated with CoCl₂·H₂SO₄ (Jones reagent, 0.5 mL) then with 3-propanol (3 mL), and the resulting orange mixture was filtered, and the filtrate was washed with water. The aqueous phase was extracted with THF, and the combined organic extracts were washed with dry THF, stoppered, and heated to 65 °C for 24 h. After the solution became homogeneous, the reaction mixture was filtered through the solution until TLC indicated complete consumption of 5.

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