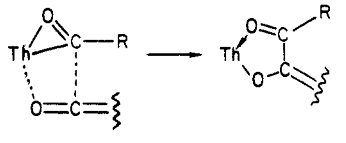
phenylphosphine to yield the ylide complexes **3** and **4**.

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, carbene 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 $Me_2C{=}CMe_2$, 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 ketenimines therefore provides a plausible model for the coupling of carbon 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). 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



(25)

for the last step of this reaction sequence is provided.

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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**, 99127-94-3; **6**, 99112-66-0; **7**, 99112-67-1; **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; $Cp_2Th(\eta^2\text{-}^{13}COCH_2\text{-}t\text{-}Bu)Cl$, 99147-67-8; $Cp_2Th(Cl)(\eta^2\text{-}COCH_2Ph)$, 99147-68-9; PPh_3, 603-35-0; PMe_3, 594-09-2; *t*-BuNC, 7188-38-7; 2,6-$Me_2C_6H_3NC$, 2769-71-3; $C_6H_{11}NC$, 931-53-3; *p*-tolNC, 7175-47-5; CO, 630-08-0; ^{13}CO, 1641-69-6; diphenylketene, 525-06-4.

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(49) The substitution of the ketenimine nitrogen atom admittedly alters the steric aspects of the lone-pair coordination.

(50) It is difficult to predict the exact degree to which species such as **O** will conform to the behavior of typical heteroatom-substituted nucleophilic carbenes (e.g., $(MeO)_2C$:). Sufficient nucleophilic character results in preferential dimerization over addition to olefins. However, monoxycarbenes such as (PhO)(H)C: are readily trapped by simple olefins such as tetramethylethylene.[15b]

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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 $NaBH_4$ and $LiAlH_4$ reductions of (1) nitriles, (2) alkenes, and (3) alkyl halides are described. (1) The kinetics of benzonitrile (PhCN) reduction indicate that at high nitrile:catalyst ratios, the rate of reduction is independent of PhCN concentration. Furthermore, the rate of PhCN reduction exhibits a first-order dependence on $NaBH_4$ concentration, as measured over a fourfold range of BH_4^- concentrations and several half-lives of PhCN. Moreover, when PhCN was reduced with equimolar mixtures of $NaBH_4$ and $NaBD_4$, 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 $NaBH_4$. (2) The selective reduction of alkenes by $NaBH_4$–$CoCl_2$ is attributed to adventitious heterogeneous catalytic hydrogenation. (3) The combination of $LiAlH_4$ with $CoCl_2$ forms a black precipitate of cobalt aluminide (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 $LiAlH_4$ 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 ($NaBH_4$) and lithium aluminum hydride ($LiAlH_4$) 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.[3,4]

More recently, the use of transition-metal catalysts or co-reagents has added new dimensions to the versatility of $NaBH_4$ and $LiAlH_4$ 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, arenes, 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.[5]

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. Homogeneous hydrogenation catalysts may be implicated, functioning with hydrogen provided by the decomposition of $NaBH_4$ or $LiAlH_4$. 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 $NaBH_4$ and $LiAlH_4$ 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 $NaBH_4$ in combination with $CoCl_2$ to reduce a nitrile to its corresponding primary amine at room temperature in CH_3OH.[6,7] A black precipitate containing >95% of the cobalt (as Co_2B) appeared, accompanied by vigorous evolution of hydrogen. Fresh supernatant from a $CoCl_2/NaBH_4$ reaction was by itself incapable of reducing benzonitrile. The boride, alone or under positive hydrogen pressure, was also excluded as the reducing agent. Furthermore, when Co_2B and benzonitrile were mixed in CH_3OH, the nitrile was found to be strongly adsorbed on the boride surface. In our preliminary communication about the mechanism of this reaction,[8] we concluded that the cobalt boride formed in situ served as a true catalyst, strongly coordinating nitriles and activating them toward reduction by $NaBH_4$. Since sodium borohydride reacted with CH_3OH at a rapid rate[9] and metal borides further accelerated this breakdown,[10] a large excess $NaBH_4$ was required to consume all the reactant.

Because $NaBH_4$ 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:H_2O was treated with excess $NaBH_4$ and Co_2B (0.1 mol·equiv *prepared in* CH_3OH), only small quantities of benzylamine were produced. Substituting a comparable amount of $CoCl_2$ for Co_2B 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 Co_2B 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 Co_2B in 2:1 THF:H_2O and avoids the harshly acidic workup of past procedures.[7]

Besides sodium borohydride, certain amine boranes like *tert*-butylamine–borane (TAB) could be used to reduce nitriles in CH_3OH in the presence of Co_2B, 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 $NaBH_4$. 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 $NaBH_4$ and Co_2B in CH_3OH became basic (pH 8.5–9.0) during borohydride decomposition, solutions of TAB in CH_3OH with Co_2B proved stable, evolving negligible quantities of H_2 and remaining neutral. When the pH of TAB–CH_3OH solutions was brought to ca. 8–9 with $NaOCH_3$ (no H_2 evolution), the reduction of benzonitrile to benzylamine became catalytic in Co_2B. This method should prove valuable in selective synthetic transformations where indiscriminate use of $NaBH_4$ must be avoided.

We next examined the role of $NaBH_4$ in nitrile reductions. Although early experiments indicated that nitriles were adsorbed on the boride surface prior to reduction, they could not distinguish whether free $NaBH_4$ 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 borohydrides,[11] heterogeneous M–H species, or transient quantities of surface-generated BH_3. Several of these might be differentiated by straightforward kinetic measurements. Assuming that the rate-determining step is early (i.e., that the reduction of intermediate imines or metalloimines is fast), then the effect of varying nitrile and borohydride concentrations and/or the observation of a kinetic isotope effect with $NaBD_4$ might shed light on the hydride-transfer process. Difficulties in working with a heterogeneous system forced us to make several minor experimental modifications in order to measure rates reproducibly. Most important was changing the solvent from methanol to ethanol to slow down the rate of uncatalyzed $NaBH_4$ decomposition. Thus fresh Co_2B (10 mol % based on nitrile) was prepared in situ for each experiment and the disappearance of benzonitrile was monitored by GLC with *n*-decane as an internal standard. Since we were hoping to observe large rate effects, we decided to measure the

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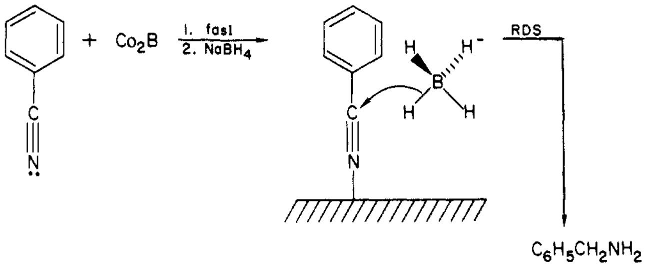
half-life of benzonitrile under various reduction conditions rather than attempt to determine rate constants with a high degree of precision. Our findings can be summarized as follows.

(1) At nitrile: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 nitrile to catalyst as a prerequisite for reduction.

(2) The rate of benzonitrile reduction exhibited a first-order dependence on $NaBH_4$ concentration, as measured over a fourfold range of $NaBH_4^-$ concentrations and several half-lives of PhCN.

(3) When benzonitrile was reduced with equimolar mixtures of $NaBH_4$ and $NaBD_4$, the product was shown by mass spectrometry to contain 58.5% d_0, 35.2% d_1, and 6.3% d_2 benzylamine. Assuming that *both* hydride addition steps leading to amine are subject to comparable isotope effects, the data are consistent with a k_H/k_D 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 $NaBH_4$ might form some "cobalt hydride" along with transient, surface-bound BH_3 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 borane was involved.[12] We have shown that cobalt boride does indeed alter the normal mode of BH_4^- decomposition in water or alcohol.[15] However, since nitrile reductions maintain a first-order dependence on borohydride even at high BH_4^- concentrations, a rate-determining decomposition of $NaBH_4$ would require an extremely weak affinity of BH_4^- 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* $NaBH_4$ as pictured below.



Alkene Reductions Using Cobalt Boride. Many transition-metal salts promote the reduction of alkynes and alkenes by $NaBH_4$.[5] Recently two reports on cobalt-based systems appeared. In 1979 Chung reported that alcoholic $NaBH_4$–$CoCl_2$ could selectively reduce alkynes as well as mono- and disubstituted alkenes in the presence of more highly substituted olefins.[16] 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 $NaBH_4$ with $CoCl_2$ produced either "CoH_2" (in THF:CH_3OH) or "BH_3" (in THF).[17] Selective hydrogenation of mono- and disubstituted alkenes in CH_3OH 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 alkanols with H_2O_2–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[16] with ethanolic $CoCl_2/NaBH_4$ could equally well be achieved under heterogeneous conditions with preformed Co_2B and H_2 gas. The boride alone (1 equiv) was incapable of reducing limonene. Homogeneous hydrocobaltation may be considered unlikely since $CoCl_2$ formed Co_2B so rapidly that "CoH_2" species would be fleeting intermediates at best. Nucleophilic attack by $NaBH_4$ on a homogeneous alkene–cobalt complex also seemed improbable for the same reasons. While it is conceivable that $NaBH_4$ might attack a heterogeneous alkene–Co_2B complex, the fact that limonene could not be reduced over Co_2B with $NaBH_4$ or $LiBH_4$ in either THF or 12:1 THF:CH_3OH (where H_2 evolution is suppressed) rendered this a remote possibility. Heterogeneous hydrogenations over both cobalt and nickel boride are, in fact, well-precedented.[18,19] In the Chung system,[16] it would appear that $NaBH_4$ is functioning solely as a source of H_2 via decomposition over Co_2B.

We also reinvestigated the combination of undissolved $NaBH_4$ (2 mol·equiv) with solid $CoCl_2$ suspended in anhydrous THF, which was reported to generate BH_3.[17] 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 BH_3 were generated, it would have reacted with dissolved $CoCl_2$ to form more boride. Transient BH_3 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 BH_3 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 $LiAlH_4$ 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 alkenes, alkynes, and alkyl halides in tetrahydrofuran solution.[20] Of these, only the $CoCl_2$-, $NiCl_2$-, and $TiCl_3$-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 $LiBH_4$ and $LiAlH_4$ in diethyl ether.[21] Excess $LiAlH_4$ reacted with $CoBr_2$ to give 4 mol·equiv of hydrogen and a black, pyrophoric precipitate which contained all the aluminum. The precipitate, designated "cobalt aluminide" ($CoAl_2$), reacted with methanol to form trimethoxyaluminum and a new

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(12) (a) Experiments with 2-aminopyridine or 1,5-cyclooctadiene, which can trap BH_3 as the corresponding amine–borane (ref 13) or 9-alkoxy-9-borabicyclo[3.3.1]nonane (ref 14) adducts, respectively, gave inconclusive results. Data analysis was complicated by adsorption of scavengers on the catalyst which interfered with the surface binding of nitrile and borohydride. (b) Adding excess BH_3–THF complex to mixtures of benzonitrile and cobalt boride in CH_3OH produced no benzylamine whatsoever, indicating the very short lifetime of this reagent in alcohol solvents.

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(15) Sodium borohydride decomposes in water or alcohol ultimately to form hydrogen and boric acid (or esters). While 2-aminopyridine alone has no effect whatsoever on the rate or course of this process, adding the amine plus $CoCl_2$ or Co_2B results in the formation of significant quantities of 2-aminopyridine borane (see ref 12).

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Table I

halide	reagents[a,b]	→	recovered SM	**5**	yield of *tert*-butylcycloheane	[*3*:*4*:unlabeled]
1	$LiAlD_4/THF$		37%	7%	56%	[0:94:5.8]
1	$LiAlD_4/CoCl_2/THF$		4.7%	2.6%	93%	[4.2:12:83.8]
2	$LiAlD_4/THF$		57%		43%	[91.3:0:8.4]
2	$LiAlD_4/CoCl_2/THF$		15%	2.2%	83%	[14.1:2:83.9]

[a] All reactions were conducted for 48 h at 65 °C in THF under Ar. [b] In runs containing $CoCl_2$, 0.1 mol·equiv was used.

black suspension of finely divided cobalt, as given in the equations below.

$$CoBr_2 + 2LiAlH_4 \rightarrow CoAl_2 + 2LiBr + 4H_2 \qquad (1)$$

$$CoAl_2 + 6CH_3OH \rightarrow 2(CH_3O)_3Al + Co + 3H_2 \qquad (2)$$

$$Co + 2H^+ \rightarrow Co^{2+} + H_2 \qquad (3)$$

This synthesis of cobalt aluminide was reproduced exactly as described, and by analyzing the precipitate with argon plasma emission spectroscopy an empirical formula of $CoAl_{1.6}$ 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 $LiAlH_4$ 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 ($CoAl_{1.1}$). 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 cyclohexane in 12% yield along with starting material (71%). In the presence of $CoCl_2$ (0.1 equiv), hydrogen was evolved and cyclohexane (64%) plus 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.

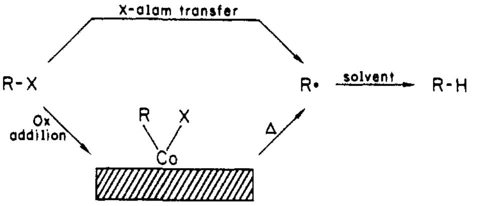
Controls established that fresh supernatant prepared in this fashion contained only residual $LiAlH_4$ and no new soluble reducing agent. When washed cobalt aluminide (10 mol %) was suspended with bromocyclohexane in fresh THF, cyclohexane (ca. 20%) was formed very sluggishly. However, if $LiAlH_4$ was added to the mixture of cobalt aluminide and bromocyclohexane, the yield of cyclohexane 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.

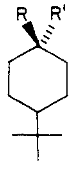
To determine the stereochemistry of cobalt aluminide mediated alkyl halide reductions, pure samples of both *cis*- and *trans*-4-bromo-*tert*-butylcyclohexane (**1** and **2**, respectively)[22] were exposed to $LiAlD_4$ in THF, with and without $CoCl_2$. Products were analyzed by gas chromatography (GC), deuterium NMR, and mass spectrometry (MS). For reference, authentic samples of *cis*- and *trans*-4-*tert*-butylcyclohexane-*1*-d_1 (**3** and **4**) were prepared as described by Wiseman, who has also reported their ^2H NMR spectra.[23] The results of this investigation are summarized in Table I.

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_1:d_0 cycloalkane were detected by mass spectrometry, corresponding closely to the deuterium content of the reducing agent. Moreover, ^2H NMR indicated complete inversion had occurred. Traces of 4-deuterio-1-butanol (resulting from competing reduction of THF) were also detected by GC, MS, and ^2H NMR.

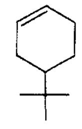
Scheme I. Mechanism of Alkyl Halide Reduction



Reduction of **1** and **2** by $LiAlD_4$ in the presence of $CoCl_2$ (0.1 equiv) gave unexpectedly different results. The product *tert*-butylcyclohexane from both **1** and **2** was 83–84% undeuterated and ca. 16% monodeuterated at C4. In each case ^2H 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 unlabeled 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 each reduction mixture confirmed the presence of a solvent dimer, most likely **6**.



1, R=Br; R'=H
2, R=H; R'=Br
3, R=D; R'=H
4, R=H; R'=D
7, R=Br; R'=D



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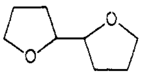

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Two plausible mechanisms (see Scheme I) for a radical-type reduction pathway are (i) halogen atom transfer from the alkyl halide to a metal radical on the aluminide surface[24] or (ii) oxidative addition of the cobalt catalyst into the carbon–halogen 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

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(24) Herrick, R. S.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* **1985**, *4*, 42 and references cited therein.

(25) (a) "B_{12}"; Dolphin, D., Ed.; Wiley: New York, 1982. (b) Vitamin B_{12}, Proceedings of the European Symposium, 3rd, 1979.

(26) $LiAlH_4$ might also reduce intermediate alkylhalides, formed by the oxidative addition pathway, to alkylcobalt hydrides. Subsequent reductive elimination to the product alkane might explain why some d_1 products are produced with stereochemical retention in the reduction of **1** and **2** by $LiAlD_4$–$CoCl_2$ (see Table I).

halide was reduced to a 43:57 mixture of **3** and **4**. This unambiguous experiment is only consistent with a heterogeneous, radical pathway for the reduction of alkyl halides by $LiAlH_4$–$CoCl_2$. The reduction of haloalkanes with $LiBH_4$–CoAl probably involves a similar mechanism.

Conclusion

Many transition metals catalyze the reduction of functional groups which are inert to $NaBH_4$ or $LiAlH_4$ alone. Moreover, several large-scale commercial processes rely on hydride-reduced transition-metal catalysts.[26] 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 aluminum hydride mediated transformations.

Experimental Section

General. Reagent grade methanol and absolute ethanol were used without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone prior to use. Benzonitrile and all alkyl halides were also distilled prior to use. Anhydrous $CoCl_2$, lithium borohydride, sodium borohydride, and lithium aluminum hydride were obtained from Alfa-Ventron Corp. Cobalt chloride hexahydrate was obtained from Fisher Chemical Co. For $CoAl_x$ reactions, stock solutions of $LiAlH_4$ 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 Villieras.[28] Stock solutions (saturated; 0.025 M) of anhydrous $CoCl_2$ in dry THF were prepared and stored in similar fashion. All reactions were conducted under Ar or N_2 unless otherwise noted. A Sage Model 341 motor drive was used as a syringe pump. Proton NMR spectra of $CDCl_3$ solutions were recorded on a Bruker WM-300 or Varian XL-200 spectrometer at room temperature. Proton-decoupled ^2H 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 (T_1) experiments were run to determine adequate delays for accurate integrations. Gas-liquid chromatography of benzonitrile, bromocyclohexane, and 1-chlorodecane was performed on a Hewlett-Packard (H-P) 5750 instrument equipped with a Spectro-Physics Minigrator. 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 benzonitrile and *n*-dodecane for 1-chlorodecane and bromocyclohexane. GLC analysis of 4-bromo-*tert*-butylcyclohexanes was performed on an H-P 5890 instrument equipped with an H-P 3392A integrator, using a Quadrex 25m, 0.32-μm ID, SE-30 (0.5-μm film) capillary column. GLC response factors for reactants and products were determined to ensure accurate yield calculations. Routine chemical ionization mass spectra (isobutane) were obtained on an AEI MS-902 mass spectrometer. All deuterated samples were analyzed in triplicate on a Finnigan 3300 gas chromatograph–mass spectrometer with electron impact ionization. Authentic undeuterated samples were also analyzed in triplicate to correct for ^{13}C contributions in the deuterated samples.

Optimum Reduction of Nitriles Using $NaBH_4$ and $CoCl_2$ in 2:1 THF:H_2O. The following is a representative procedure. A pink solution of $CoCl_2 \cdot 6H_2O$ (0.445 g, 1.87 mmol) and benzonitrile (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 $NaBH_4$ (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 $NaBH_4$ (0.41 g) was added. After a total time of 2 h, 28% NH_4OH solution (2 mL) was added and the mixture transferred to centrifuge tubes. After centrifugation the supernatant (two liquid phases) was decanted and the sediment washed with more of the same solvent mixture. The combined supernatants were concentrated at reduced pressure to remove the bulk of THF, then the aqueous residue was extracted with 4 × 40 mL of CH_2Cl_2. The combined CH_2Cl_2 layers were dried ($MgSO_4$) 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 $^5/_8 \times {}^5/_{16}$ in. magnetic stirbar was added a solution of $CoCl_2 \cdot 6H_2O$ (0.179 g, 0.75 mmol) in ethanol (35 mL). After the sample was equilibrated in a 23.0 °C water bath, a solution of $NaBH_4$ (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 Co_2B formed. After 15 min, a solution of benzonitrile (0.775 g, 7.5 mmol) and *n*-decane (0.194 g) in ethanol (10 mL) was added. The flask and contents were equilibrated for 15 min, then finely pulverized $NaBH_4$ (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:EtOH). Each aliquot was shaken vigorously to decompose both $NaBH_4$ and Co_2B and then centrifuged and the supernatant was analyzed by GLC.

Each run was performed in duplicate and monitored for 2 h. Concentrations of both $NaBH_4$ and benzonitrile were varied as shown below. In the run where the benzonitrile concentration was doubled, the quantity of decane added was doubled as well. Control experiments in which no solid $NaBH_4$ was added to mixtures of PhCN and Co_2B showed that less than 1% reduction had occurred after 2 h. Results ([$NaBH_4$], [PhCN], $T_{1/2}$ ($T_{1/2}$ is the time required for one-half the benzonitrile to be consumed)):

0.30 M	0.15 M	1700 ± 250 s
0.60 M	0.15 M	950 ± 150 s
0.30 M	0.30 M	3150 ± 350 s

Competitive Reductions with $NaBH_4$/$NaBD_4$. Run 1. To a rapidly stirred solution of $CoCl_2 \cdot 6H_2O$ (0.179 g, 0.75 mmol) in absolute ethanol (35 mL) was added a fresh solution of $NaBH_4$ (0.064 g, 1.70 mmol) in EtOH (5 mL) over 130 s by syringe pump. The reaction flask was kept at 23 ± 1 °C in a water bath. After 15 min an intimate mixture of finely pulverized $NaBH_4$ (0.550 g, 14.6 mmol) and $NaBD_4$ (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 taken up in water (25 mL). The pH was adjusted to 9.0 with 4 M NaOH, and then the aqueous phase was extracted with four 15-mL portions of $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered, and then evaporated to give 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 $NaBH_4$ (0.734 g, 19.4 mmol) and $NaBD_4$ (0.821 g, 19.4 mmol).

Both runs afforded material whose 300-MHz ^1H NMR spectrum matched that of an authentic sample of benzylamine. Electron impact mass spectral analysis of the deuterated amine mixtures was best accomplished after acetylation. The results were as follows: run 1, d_0, 57.5%; d_1, 36.1%; d_2, 6.4%; run 2, d_0, 59.6%; d_1, 34.3%; d_2, 6.1%.

Assuming comparable isotope effects for the two hydride addition steps, d_0:d_1:d_2 ratios were calculated for various isotope effect values and compared to the experimentally determined ratios. The best mean-square fit with experiment are the following: run 1, 3.15 ± 0.39; run 2, 3.42 ± 0.62; average = 3.29 ± 0.50.

Selective Alkene Reductions Using Co_2B–H_2. To a 25-mL round-bottomed flask equipped with stirbar was added freshly made Co_2B (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 H_2 for 12 h. The reaction mixture was acidified (3 N HCl, 10 mL) to decompose the boride and the product extracted with 3 × 15 mL of ether. The combined extracts were washed with water (10 mL) and brine (10 mL) and then dried over $MgSO_4$ and filtered. Concentration in vacuo afforded 4-isopropyl-1-methyl-1-cyclohexene in 85% yield along with 15% of recovered limonene.

Analysis of $CoAl_x$. To an oven-dried 50-mL round-bottomed centrifuge tube equipped with a $^1/_2$ in. stirbar was added a solution of anhydrous $CoCl_2$ in THF (30 mL of a 0.024 M solution, 0.73 mmol). The flask was cooled to −40 °C in a dry ice–acetonitrile bath, and then dissolved $LiAlH_4$ (1.6 mL of a 0.45 M solution, 0.73 mmol) was added over 1 min with stirring. The solution turned black and H_2 was evolved. After 85 min the mixture was centrifuged and the colorless supernatant removed by syringe and discarded. Fresh THF (5 mL) was added, the mixture briefly stirred and centrifuged, and the supernatant discarded. This washing procedure was repeated four times then the residual black solid was decomposed by cautious addition of 0.1 N HCl (15 mL). The pink solution was serially diluted and analyzed in triplicate by argon plasma emission spectroscopy for both Co and Al.

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Partitioning the $LiAlH_4/CoCl_2$ 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 $CoCl_2$ (0.05 mmol in 2 mL of THF). Lithium aluminum hydride (0.074 mmol in 0.21 mL of THF) was added without stirring and a black deposit of $CoAl_x$ appeared instantly. After 30 min the vial was centrifuged and the brownish 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 $CoAl_x$ was washed with dry THF (2 mL).

To the tubes containing clear supernatant and washed aluminide 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 $LiAlH_4$. 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. The results for duplicate runs were as follows:

		cyclohexane	bromocyclohexane
run 1:	supernatant	21%	66%
	aluminide	85%	13%
run 2:	supernatant	20%	70%
	aluminide	89%	11%

When the aluminide prepared exactly as above was heated alone with bromocyclohexane (24 h, 65 °C in THF, no $LiAlH_4$ added), GLC analysis revealed 21% cyclohexane and 79% bromocyclohexane.

Reduction of 1-Chlorodecane with $CoAl_x$ and $LiBH_4$. An oven-dried 10-mL Kimble vial fitted with septum and stirbar containing $CoCl_2$ (0.017 g, 0.13 mmol) in THF (5 mL) was treated with $LiAlH_4$ (1.40 mL of a 0.14 M solution in THF). After 5 min the reaction mixture was centrifuged and the colorless supernatant discarded. The black precipitate was washed twice with dry THF (1.5 mL) and then treated with 1-chlorodecane (0.018 g, 0.10 mmol in 1.2 mL of THF) and $LiBH_4$ (4.9 mL of a 0.04 M solution in THF; 0.20 mmol). The vial was tightly stoppered and then heated to 65 °C for 24 h. After the mixture was cooled, water (5 drops) and dodecane (0.017 g) were added. The THF was dried ($MgSO_4$) and the product analyzed by GLC. The yield of *n*-decane was 52% and that of 1-chlorodecane was 32%.

Reduction of *cis*- and *trans*-4-Bromo-*tert*-butylcyclohexanes (1 and 2) with $CoAl_x$ and $LiAlD_4$. Identical reductions were performed on **1** and **2**. To a stock solution of $CoCl_2$ (6.5 mg, 0.05 mmol in 2 mL of dry THF) in a flame-dried, 10-mL Kimble vial equipped with rubber septum and stirbar was added without stirring a solution of $LiAlD_4$ (3.2 mg, 0.075 mmol) in THF (0.12 mL). Gas was evolved and a black precipitate formed. After standing at room temperature for 30 min and stirring for 30 min, the mixture was centrifuged, the supernatant discarded, the precipitate washed once with dry THF (1 mL), and the supernatant again discarded. To the washed, centrifuged aluminide was added a solution of the bromide (0.109 g, 0.50 mmol) in THF (1 mL) followed by a solution of $LiAlD_4$ (0.021 g, 0.50 mmol in 0.82 mL of THF) plus additional THF (3.18 mL). The vial was then stoppered and heated to 65 °C for 48 h. After the vial was cooled, water (ca. 2 mL) was cautiously added dropwise to decompose the $LiAlD_4$ and $CoAl_x$. The aqueous phase was extracted with pentane (3 × 3 mL) and the combined organic extracts washed with water (5 mL), dried ($MgSO_4$), and concentrated to afford 0.095 g of a colorless oil. Product analyses from **1** and **2** are listed in Table I.

Control reductions of **1** and **2** with $LiAlD_4$ alone were performed as above in the absence of $CoCl_2$.

Preparation of *trans*-4-Hydroxy-4-deuterio-*tert*-butylcyclohexane. Following an "Organic Syntheses" procedure for the corresponding $LiAlH_4$ reduction,[28] 4-*tert*-butylcyclohexanone (23.5 g, 0.152 mol) was treated with $LiAlD_4$ (2.00 g, 47.6 mmol; 98% atom D; Alfa-Ventron) and $AlCl_3$ (22.29 g, 0.167 mol) in ether at reflux. Workup as published afforded 23.25 g of oil. The crude product was taken up in pentane (100 mL) and cooled to −78 °C whereupon crystals appeared of *trans*-4-hydroxy-4-deuterio-*tert*-butylcyclohexane (11.19 g). The supernatant contained additional less pure product (8.25 g; total yield 82%): ^1H NMR δ 1.97 (d, 2 H, $J = 12.1$ Hz), 1.76 (d, 2 H, $J = 9.2$ Hz), 0.86–1.6 (m, 6 H), 0.82 (s, 9 H); ^2H NMR ($CDCl_3$) δ 3.46 (s); IR ($CHCl_3$) 3620, 3440, 3010, 2985, 2765, 2120 (ν_{C-D}), 1482, 1470, 1455, 1395, 1370, 1120, 1080 cm^{-1}; EIMS 157 (M^+, 0.3%), 139 ($M^+ - H_2O$, 19%).

Preparation of *cis*-4-Bromo-4-*tert*-butylcyclohexane. To an oven-dried, 300-mL, round-bottomed, three-necked flask fitted with thermometer, septum, and mechanical stirrer was added triphenylphosphine (17.5 g, 66.8 mmol) and acetonitrile (64 mL). Bromine (3.42 mL, 66.8 mmol) was added by syringe over 10 min to the rapidly stirred mixture with use of a cold-water bath to hold the reaction mixture between 20 and 30 °C. Solid *trans*-4-hydroxy-4-deuterio-*tert*-butylcyclohexane (10 g, 63.6 mmol) was added in one portion. Within 5 min, the pale yellow reaction mixture became homogeneous. After 1 h, by which time GLC analysis indicated that the reaction was complete, the reaction mixture was poured into water (200 mL), causing a viscous oil to precipitate. The aqueous supernatant was extracted with hexane (4 × 100 mL). When the viscous 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 **7** contaminated with alkene **5** were eluted with hexanes. These were redissolved in acetone, cooled to −78 °C, and a stream of ozone passed through the solution until TLC indicated complete consumption of **5**. The reaction mixture was warmed to room temperature and treated with $CrO_3–H_2SO_4$ (Jones reagent, 0.5 mL) then with 2-propanol (3 mL), and the resulting chromium salts were filtered. Concentration afforded a green oil which was chromatographed as before to furnish pure **7** (1.59 g, 11%) as a colorless oil. Further purification by low-temperature crystallization from pentane afforded 1.10 g of **7** (mp ca. 20 °C), judged to be 99.4% pure by GLC analysis: ^1H NMR δ 2.11 (d, 2 H, $J = 14.7$ Hz), 1.67–1.79 (m, 2 H), 1.52–1.60 (m, 4 H), 0.96–1.07 (m, 1 H), 0.82 (s, 9 H), ^2H NMR ($CDCl_3$) δ 4.62 (s); IR ($CHCl_3$) 2980, 2880, 2865, 2220 (ν_{C-D}), 1490, 1480, 1450, 1430, 1400, 1370, 1320, 1250, 1240, 1190, 1110, 1010, 900 cm^{-1} cm^{-1}, EIMS 140 (M − HBr, 100%).

Reduction of 7 Using Cobalt Aluminide in THF. In an oven-dried 25-mL screw-top vial, a stock solution of $CoCl_2$ in THF (0.025 M, 20 mL; 0.50 mmol) was reduced with $LiAlH_4$ (1.0 mL of a 0.75 M THF solution; 0.75 mmol) and washed thoroughly with THF as described above ("Analysis of $CoAl_x$"). The resulting CoAl was suspended in fresh THF (1 mL) and to it was added bromide **7** (0.110 g, 0.50 mmol in 1 mL of THF). The reaction volume was brought to 5 mL with dry THF, the septum replaced with a tightly clamped polyethylene cap, and the vial heated in a 65 °C oil bath for 24 h. Water (2 mL) was added, the contents stirred for 2 h to decompose all the black solid, and the aqueous layer extracted with pentane (3 × 3 mL). GLC analysis at this point revealed only *tert*-butylcyclohexane along with the solvent dimer. The combined pentane extracts were washed with water (5 mL), dried ($MgSO_4$), filtered, and concentrated to afford a colorless oil (42 mg, 60%). Mass spectral analysis indicated the product to be 96.9% d_1 and 3.1% d_0 *tert*-butylcyclohexane. Product analysis by ^2H NMR indicated the presence of **3** and **4** in a 43:57 ratio, corresponding to 43% inversion and 57% retention of configuration.

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