Figure 1c shows a 2-D correlated spectrum of I with use of a triple quantum filter. In agreement with expectations, the methyl peak is absent as there is only one resolved coupling to CHBr. In the weak coupling approximation of a linear $A_2M_2RX_3$ coupling network, no cross-peaks should appear at all for triple or higher quantum filtering. However, the weak chemical nonequivalence of the CH_2 groups and the violation of the weak coupling condition ($\delta/J \simeq 16$) allow the appearance of cross-peaks between the two CH_2 groups. Due to the restriction of coherence transfer through certain orders of multiple quantum coherence, the sensitivity is somewhat reduced. For example, a double quantum filter reduces the cross-peak amplitudes by a factor 2 (compare Figure 1a and b with a total of 4 and 16 scans, respectively).

Higher order multiple quantum filters gradually decrease the complexity of 2-D spectra and focus attention on spin systems with intricate coupling networks. This feature can also be utilized to simplify 1-D proton spectra by inserting a multiple quantum filter in the excitation sequence, for example in the form: $90°(\varphi)-\tau-180°(\varphi)-\tau-90°(\varphi + \psi)-90°$-acquisition ($\psi = 0$ for p even and $\psi = \pi/2$ for p odd). In this way, transitions of spin subsystems with accessible multiple quantum transition of order p are excited exclusively. For example, a four-quantum filter eliminates, in addition to all one-, two-, and three-spin systems, all linear coupling networks of the type ··A-B-C-D···.[11] Multiple quantum filters have the potential to facilitate the analysis of complex spin systems while retaining the accustomed data presentation form of standard 2-D and 1-D NMR spectroscopy.

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The Mechanism of Sodium Borohydride–Cobaltous Chloride Reductions

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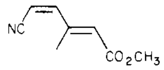
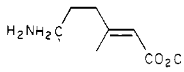
The combination of sodium borohydride with cobalt(II),[1] nickel(II),[1,2] copper(II),[3] and rhodium(III)[4] halides has been employed to reduce functional groups such as nitriles, amides, and olefins,[3,5] which are inert to $NaBH_4$ alone. Despite frequent use,[6–15] the nature of the actual reducing species in these complex mixtures remains obscure. For example, the reaction of $NaBH_4$ with $CoCl_2$ in CH_3OH is exothermic and instantly deposits a black granular precipitate of cobalt boride (Co_2B)[16–18] while steadily evolving hydrogen. Conceivable reducing agents in such a mixture, to name only a few, include (a) the heterogeneous Co_2B/H_2 system, which is known to hydrogenate olefins and nitriles,[19] (b) homogeneous cobalt hydrogenation catalysts,[20] or (c) soluble cobalt borohydride complexes,[17–21] some of which constitute good hydride donors. Herein we report experiments that rule out the above mentioned possibilities and strongly suggest that cobalt boride, by coordinating to certain functional groups, catalyzes their heterogeneous reduction by $NaBH_4$. This understanding has led to the rational design of a superior reagent, $Co_2B/t\text{-}BuNH_2{\cdot}BH_3$, for more efficient, selective reduction of nitriles.

Table I. Catalytic $Co_2B/NaBH_4$ Reductions

substrate	conditions[a]	product (yield, %)
PhCN	A, B; rt, 4 h	$PhCH_2NH_2$ (79–85)
$PhCH_2CN$	A, rt, 2 h	$PhCH_2CH_2NH_2$ (74)
 **1**	A, 0 °C, 8 h[b]	 **2** (60)[c]
$PhCONH_2$	A, reflux, 36 h	$PhCH_2NH_2$ (8) (see ref 23)
$PhCH{=}CHCO_2CH_3$	B, rt, 2 h	$PhCH_2CH_2CO_2CH_3$ (85)
$CH_3(CH_2)_5C{\equiv}CH$	A, rt, 3 h	octane (83)

[a] Conditions: A, Co_2B (1 equiv) + $NaBH_4$ (5–10 equiv) in CH_3OH; B, Co_2B (0.1 equiv) + $NaBH_4$ (5 equiv) in CH_3OH; rt = room temperature. [b] Ethylenediamine (5 equiv) was added to this reaction mixture. [c] $NaBH_4$ alone reduced the double bond but not the nitrile.

When $CoCl_2$ was treated with 5 mol equiv of $NaBH_4$ in CH_3OH for 10 min, 95% of the cobalt was deposited as Co_2B, an air-stable solid that could be isolated by filtration.[22] Two experiments demonstrated that the residual dissolved cobalt was most likely a Co(II) species. Adding more $NaBH_4$ precipitated further traces of Co_2B; moreover, supernatant acidified with HCl turned the faint blue characteristic of $CoCl_2$. A weighed sample was reexposed to $NaBH_4/CH_3OH$ with negligible catalyst decomposition to show that the boride was stable to the reduction conditions; again, only traces of leached soluble cobalt(II) salts were detected.

Fresh supernatant from a $CoCl_2/NaBH_4$ reaction was by itself incapable of reducing benzonitrile. The boride alone, although known to occlude some H_2 during its formation,[16] was also ruled out as the reducing agent. However, when equimolar quantities of benzonitrile and Co_2B were mixed, we unexpectedly found most of the nitrile to be strongly adsorbed on the solid surface; it could be released by ammonolysis (28% NH_4OH) or by dissolving the boride in aqueous HCl. Control hydrolyses further demonstrated that Co_2B bound to benzonitrile easily survived acidic conditions that otherwise decomposed the pure boride, or boride containing benzylamine. This protective effect exerted by nitriles has not been noted before.[23]

When Co_2B (0.2 equiv) in CH_3OH was stirred under 1 atm of H_2 with either benzonitrile or benzamide, no benzylamine was observed, even after 11 days. Altogether these experiments strongly suggested that neither adsorbed H_2, exogenous H_2, nor soluble cobalt-containing boron hydride species played any sig-

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(22) Caution: Co_2B becomes pyrophoric when dried under vacuum (6 h). It can be air-dried but is most safely stored moist with solvent.

(23) In contrast, benzamide was not adsorbed on Co_2B to any appreciable extent, and we were unable to reproduce its reported reduction to benzylamine by using $NaBH_4/CoCl_2$.[1] Others[13] have apparently had similar difficulties with primary amides.

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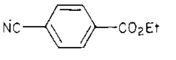
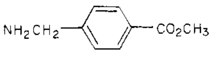
Table II. Reductions with Co_2B/TAB

substrate	conditions[a]	product (yield, %)
PhCN	2 equiv TAB, 3 h	$PhCH_2NH_2$ (75)
$PhCH_2CN$	2 equiv TAB, 7 h	$PhCH_2CH_2NH_2$ (88)
$CH_3(CH_2)_4CN$	2 equiv TAB, 2.5 h	$CH_3(CH_2)_5NH_2$ (81)
	4 equiv TAB, 12.5 h	 (75)
$PhCONH_2$	2 equiv TAB, 3 h	NR[b]
$PhCH{=}CHCO_2CH_3$	2 equiv TAB, 3 h	$PhCH{=}CHCO_2CH_3$ (75)
$CH_3(CH_2)_5C{\equiv}CH$	2 equiv TAB, 2 h	$\left\{\begin{array}{l}\text{octene}\\\text{octane}\end{array}\right\}(25)^c$ octyne (75)

[a] All reactions were run with 1 equiv of Co_2B at reflux in CH_3OH under N_2. [b] No reaction. [c] Yield determined by GC.

nificant part in the reduction of nitriles and carboxamides by this system.

Although fresh supernatant alone from $NaBH_4/CoCl_2$ mixtures did not reduce benzonitrile, some benzylamine could be produced even from aged supernatant in the presence of Co_2B. Thus a mixture of $NaBH_4$ (10 mmol) with $CoCl_2$ (2 mmol) in CH_3OH (6 mL) was stirred for 50 min until gas evolution had subsided. Benzonitrile (1 mmol) was then added, and workup afforded benzylamine (18% after 15 min; 25% after 5 h), apparently formed by residual $NaBH_4$ in a Co_2B-assisted process.

Consistent with this hypothesis, benzonitrile treated with prewashed Co_2B and then with $NaBH_4$ in CH_3OH afforded benzylamine in 85% yield.[24] Similar results were obtained with both 6-week-old and recycled samples of the boride. In fact, an efficient catalytic reduction was devised by utilizing 10 mol % of Co_2B with portionwise addition of $NaBH_4$ until TLC analysis indicated complete consumption of starting material. Cobalt boride/$NaBH_4$ rapidly converted methyl cinnamate to methyl hydrocinnamate (85%)[3] and 1-octyne to octane (83%). The latter transformation may be a catalytic hydrogenation;[19] the former clearly is not, nor is it a reaction of $NaBH_4$ alone. Prior poisoning of the catalyst with ethylenediamine[25] dramatically inhibited all these reductions. Moreover $NaBH_3CN$ could not replace $NaBH_4$ as the hydride source. Table I summarizes representative reductions.

At present our results cannot distinguish whether free $NaBH_4$ or some other, more complex reducing agent formed directly on the boride surface is the actual "hydride" donor. Among such possibilities are multinuclear, bridged borohydrides, heterogeneous Co–H complexes,[26] or even transient quantities of highly reactive, surface-generated BH_3. The chemistry of Co_2B with amine boranes was explored to evaluate this last prospect. These reducing agents are stable at ambient temperature but thermally dissociate into free BH_3.[27] When *tert*-butylamine–borane (TAB), a reagent normally inert to nitriles, was combined with benzonitrile and an equivalent of Co_2B, benzylamine was produced in high yield. Alkenes and alkynes were reduced more slowly in this system than with $NaBH_4/CoCl_2$ (Table II). Moreover a large excess of reducing agent was unnecessary since TAB decomposed only sluggishly during reduction. This new reaction should prove useful in many complex synthetic transformations.

Whatever their mechanism, these amine–borane reductions are not catalytic in the boride and must involve some complex surface phenomena besides ordinary chelation that deserves further study in aprotic media. New heterogeneous organometallic reactions under those conditions will be the subject of a future report. For the moment, our mechanistic findings should be of interest with respect to other transition-metal-assisted hydride reductions where the corresponding borides are formed in situ.

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Registry No. 1, 83462-98-0; **2**, 83462-99-1; Co_2B, 12045-01-1; *t*-$BuNH_2{\cdot}BH_3$, 7337-45-3; $NaBH_3CN$, 25895-60-7; PhCN, 100-47-0; $PhCH_2CN$, 140-29-4; $NaBH_4$, 16940-66-2; $CoCl_2$, 7646-79-9; $PhCONH_2$, 55-21-0; $PhCH{=}CHCO_2CH_3$, 103-26-4; $CH_3(CH_2)_5C{\equiv}CH$, 629-05-0; $PhCH_2NH_2$, 100-46-9; $PhCH_2CH_2NH_2$, 64-04-0; $PhCH_2CH_2CO_2CH_3$, 103-25-3; $CH_3(CH_2)_4CN$, 628-73-9; $CH_3(CH_2)_5NH_2$, 111-26-2; octane, 111-65-9; ethyl 4-cyanobenzoate, 7153-22-2; methyl 4-(aminoethyl)benzoate, 18469-52-8.

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Dihydroxamate Analogues of Rhodotorulic Acid and an Exceptional Dimer: Preparation and Crystal Structure of $Fe_2[i\text{-}C_3H_7N(O)C({=}O)({-}CH_2{-})_5\text{-}C({=}O)N(O)\text{-}i\text{-}C_3H_7]_2(\mu\text{-}OCH_3)_2$

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The siderophores are low molecular weight chelating agents that are produced by microbes to solubilize and transport ferric ion to the cell membrane.[1,2] The hydroxamate group [HON-$(R_1)(C({=}O))R_2$] is one of the most common functional groups found in siderophores produced by molds, fungi, and yeasts. The compounds are predominantly trihydroxamic acids that form extremely stable 1:1 complexes with Fe^{3+}. Rhodotorulic acid (RA, **1a**, Figure 1) is unusual among the hydroxamate siderophores in that it is a dihydroxamic acid and is thus unable to satisfy the preferred octahedral coordination geometry of Fe^{3+} by the formation of a simple 1:1 complex. We have shown that RA forms a dimeric complex in solution of stoichiometry Fe_2RA_3.[3] Unfortunately there is no experimental evidence to distinguish between proposed structure **1b** with three bridging hydroxamate ligands and alternative structure **1c**, which possesses only a single bridging ligand. Furthermore, we have been unable thus far to isolate single crystals of Fe_2RA_3 for an X-ray structural analysis.

In an effort to lend support to the triply bridged dimeric structure proposed for ferric rhodotorulate, a series of model ligands, $i\text{-}C_3H_7N(OH)C({=}O)({-}CH_2{-})_nC({=}O)N(OH)\text{-}i\text{-}C_3H_7$ (n = 3–6, 8, 10) were prepared,[4] and their coordination chemistry with Fe^{3+} was examined. Molecular models indicate that by varying the chain length between the functional groups, the distance between the metal centers in the triply bridged dimers may be systematically varied from approximately 5 to 12 Å. It was of interest to determine what effect the chain length would have on the chemical and physical properties of the dimeric complexes as the distance between the paramagnetic iron centers is adjusted.

In aqueous solution the synthetic dihydroxamate ligands form complexes with Fe^{3+} that are analogous to the RA complex over the entire range of chain lengths.[5] The formation constants per

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[5] Analytical data are consistent with $Fe_2L_3{\cdot}H_2O$ when isolated from solutions with Fe:L = 2:3. Solid complexes appear to be polymeric; however molecular weight measurements (gel partition chromatography in H_2O and MeOH) are consistent with a dimeric formulation.

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