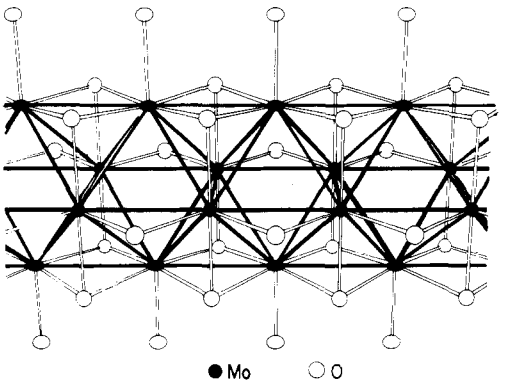

Figure 2. A view of one cluster chain, $[Mo_2Mo_{4/2}O_2O_{8/2}^-]$, extended parallel to the c axis. The repeat distance along the chain is 2.860 (1) Å.

Another interesting feature of this structure is the site occupied by Na^+ ions within the channels. Each Na^+ ion is surrounded by eight oxygen atoms at a distance of 2.740 (8) Å in tetragonal symmetry.[18] The Na-O distance is ~0.39 Å longer than the sum of ionic radii (2.35 Å) and accordingly the Na^+ ions exhibit unusually large isotropic thermal parameters, 7.2 (9) Å^2. This feature suggests that still larger cations can be accommodated in this structure and that the Na^+ ions indeed may be exchangeable as in the zeolites or Molecular Sieves. It also may be possible to remove the Na^+ ions altogether in an oxidative process leaving intact the Mo_4O_6 structure, or to prepare compounds $M^{n+}[Mo_4O_6^{n-}]$ with $n = 2$, 3, or 4 such that the electron/metal ratio is varied over the range 3.0–4.0. These aspects and intensive examination of properties are currently being studied in this laboratory.

Acknowledgment. We express our appreciation to Professor R. A. Jacobson and especially Mr. Douglas Powell for their valuable assistance during the X-ray structure determination. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division, under Contract No. 7405-eng-82.

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(8) In this formulation i indicates a ligand atom which occupies an inner bridging position of the cluster, and o indicates a ligand in an outer or exo position. See Schäfer, H; von Schnering, H.-G. *Angew. Chem.* **1964**, *76*, 833.
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(16) The crystals of $NaMo_4O_6$ are tetragonal, $a = 9.559$ (3), $c = 2.860$ (1) Å; $Z = 2$; $V = 261.3$ Å^3. A total of 216 reflections with $I > 3\sigma(I)$ averaged from data taken over four octants was used to solve and refine the structure. The structure was solved in the space group $P4/mbm$ and all atoms were refined to convergence using anisotropic thermal parameters. Since the transmission factor varied only from 0.85 to 0.87 over all orientations, no absorption correction was applied to the data. The occupancy of the Na positions was included as a variable in the refinement and converged to the value 1.02. The final cycle of least-squares refinement provided $R_1 = 0.046$ and $R_2 = 0.054$.
(17) Subsequent work has shown that essentially pure $NaMo_4O_6$ can be prepared in the reaction $Na_2MoO_4 + 4MoO_2 + 3Mo = 2NaMo_4O_6$ when the stoichiometric quantities of Na_2MoO_4 and MoO_2 are heated in a sealed Mo tube at 1100 °C for 7 days. The X-ray diffraction powder pattern of this preparation was identical with that of the single crystals.
(18) The eight O atoms in the coordination sphere of Na^+ form a cube compressed along the c axis with O–O distances of 2.860 and 3.304 Å.

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An Unexpected Hydride Transfer Reaction of Hydridoborates. A Convenient New Route to Highly Hindered Potassium Trialkylhydridoborates[1a]

Sir:

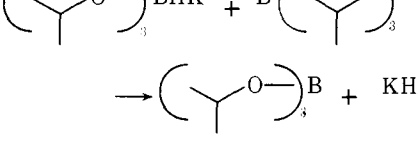
Potassium triisopropoxyhydridoborate $[KHB(O\text{-}i\text{-}Pr)_3]$,[1b] a "mild" reducing agent,[1c] transfers hydride rapidly and quantitatively to both simple and highly hindered trialkylboranes to form potassium trialkylhydridoborates ($KHBR_3$), reducing agents of exceptional activity and nucleophilicity. $KHB(O\text{-}i\text{-}Pr)_3$ is readily formed from potassium hydride (KH) and triisopropoxyborane $[B(O\text{-}i\text{-}Pr)_3$, "isopropylborate"]. Thus the observed hydride transfer provides a convenient new route to highly hindered potassium trialkylhydridoborates from trialkylboranes which fail to react with KH.[1d] In addition, it provides an unprecedented example of nonsteric kinetic factors inhibiting the apparent reducing power of a hydridoborate.

Hydridoborates have achieved widespread use as reducing agents. Virtually no systematic comparisons exist among the various hydridoborates to delineate relative reactivities. However, certain trends may be deduced.

Some years ago it was reported that replacement of hydride by alkoxide in sodium tetrahydroborate ($NaBH_4$) appeared to facilitate transfer of the remaining hydride(s).[2,3] Thus $NaHB(O\text{-}i\text{-}Pr)_3$ was found to be more reactive toward organic carbonyl compounds in ether solvents. Similarly, $KHB(O\text{-}i\text{-}Pr)_3$ is far more reactive toward reduction of methyl iodide in ether solvents than is $NaBH_4$,[4] and it reduces metal carbonyl complexes with greater facility than does $NaBH_4$.[5]

Recently, a variety of trialkylhydridoborates[6] have been shown to be highly reactive as reducing agents in organic[6,7] and organometallic[8] chemistry. These reagents appear far more reactive than $KHB(O\text{-}i\text{-}Pr)_3$. For example, trialkylhydridoborates reduce cyclic ketones readily at −78 °C or below,[7b,9] while $KHB(O\text{-}i\text{-}Pr)_3$ is very sluggish below −23 °C.[1c,4] Similarly, *n*-octyl chloride is reduced in 30–60 min at 25 °C by $MHBR_3$ (M = Li, R = Et;[10a] M = K, R = *i*-Bu[10b]), but $KHB(O\text{-}i\text{-}Pr)_3$ is inert toward *n*-octyl chloride at room temperature.

These observations clearly indicate an order of reactivity $HBH_3^- < HB(OR)_3^- < HBR_3^-$. Thus it was highly surprising to observe that trialkylhydridoborates failed to convert trialkoxyboranes to trialkoxyhydridoborates. In fact, the opposite reaction occurred with great ease. Addition of $(i\text{-}Bu)_3B$ [isostructural with $(i\text{-}PrO)_3B$] to 1.0 equiv of $KHB(O\text{-}i\text{-}Pr)_3$ in THF solution at 25 °C resulted in rapid, quantitative hydride transfer to yield an equimolar mixture of $KHB(i\text{-}Bu)_3$ and $(i\text{-}PrO)_3B$ (eq 1), as may be seen from the ^{11}B NMR



(1)

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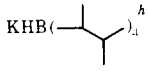
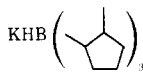
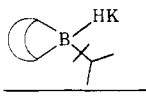
Table I. Preparation of Representative Simple and Highly Hindered Potassium Trialkylhydridoborates via Hydride Transfer

	from $KHB(OiPr)_3 + R_3B$[a]					from $KH + R_3B$[a,b]				
	reaction conditions		^{11}B NMR[c]			reaction conditions		^{11}B NMR[c]		
trialkylhydridoborate	time, min	temp, °C	chemical shift, δ	J_{B-H}, Hz	$W_{1/2}$[d], Hz	time, min	temp, °C	chemical shift, δ	J_{B-H}, Hz	$W_{1/2}$[d], Hz
$KHB(Et)_3$	<5	≤25	−12.6	62	8	<10	0	−12.5	67	9
$KHB(n\text{-}Bu)_3$	<5	≤25	−14.8[e]	62	14	<10	25	−14.8[e]	65	17
$KHB(i\text{-}Bu)_3$	<5	≤25	−17.9	69	8	<10	25	−17.9	70	12
$KHB(sec\text{-}Bu)_3$	<5	≤25	−7.1	69	14	≤60	25	−7.2	71	16
	<5	≤25	−11.9 −13.6	75 75	6 6	...[f]				
	<5	≤25	−12.3 −13.7	71 72	14 14	...[f]				
	<5	≤25	−10.3	74	11	...[g]				

[a] Addition of R_3B to THF solution of suspension (KH) of hydride transfer reagent. [b] See also ref 1b. [c] Spectra recorded using a Varian FT-80A spectrometer at 25.517 MHz. Sample solutions were ~0.25 M in $KHBR_3$. Chemical shifts are reported relative to external $BF_3{\cdot}OEt_2$ (δ 0). [d] Proton noise decoupled line width at half-height. [e] There was also a resonance at δ −12.2, presumably due to $KHB(n\text{-}Bu)_2(sec\text{-}Bu)$. [f] Cannot be formed by the direct reaction of R_3B and KH as described in ref 1b and in Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913. [g] Formed only to the extent of ~5% after 17 h at 25 °C. [h] Diastereomeric pair; area of δ −11.9/area of δ −13.6 is approximately 3:1. [i] Diastereomeric pair; area of δ −12.3/area of δ −13.7 is approximately 3:1.

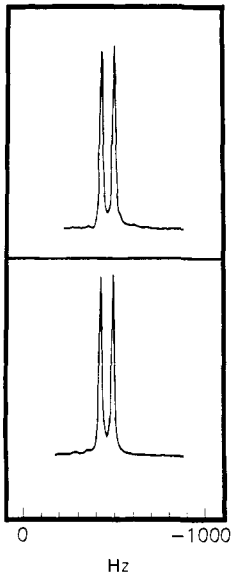


Figure 1. Upper: ^{11}B NMR spectrum of $K^{+-}HB(i\text{-}Bu)_3$ in THF prepared according to ref 1b. Lower: ^{11}B NMR spectrum of high-field signals in sample prepared by mixing equimolar solutions of $K^{+-}HB(O\text{-}i\text{-}Pr)_3$ and $B(i\text{-}Bu)_3$ in THF. Signal due to $B(O\text{-}i\text{-}Pr)_3$ is not shown.

spectra in Figure 1.

Quantitative hydride transfer is indicated by two factors. First, the resonance signals of triisobutylborane and triisopropoxyhydridoborate are absent. Second, the line shape of the triisobutylhydridoborate resonance is essentially identical with that of triisobutylhydridoborate prepared from triisobutylborane and potassium hydride; the presence of even a few mole percent of free triisobutylborane in solutions of potassium triisobutylhydridoborate causes line broadening and collapse of B-H coupling, due to rapid hydride exchange.[1e,11]

Even organoboranes with greater steric hindrance than triisobutylborane undergo rapid, quantitative hydride transfer from potassium triisopropoxyhydridoborate. In this manner, trialkylboranes too hindered to undergo direct reaction with potassium hydride are readily converted to the corresponding trialkylhydridoborates. Representative examples with widely varying steric requirements are summarized in Table I. No evidence was observed to indicate that the triisopropoxyborane remains coordinated in any way to the trialkyl hydridoborates.

This unusual hydride transfer from the "mild" reducing agent $KHB(O\text{-}i\text{-}Pr)_3$[12] to produce the "strong" reducing agents $KHBR_3$ clearly indicates that $KHB(O\text{-}i\text{-}Pr)_3$ is *thermodynamically* a more potent reducing agent than trialkylhydridoborates but is inhibited by powerful nonsteric kinetic factors. Such differences between thermodynamic and kinetic hydride transfer ability do not appear to have been considered previously in hydridoborates.

The novel hydride transfer reaction described herein provides a convenient new route to previously inaccessible potassium hydridoborates from readily available materials. In addition, it raises new questions regarding the factors which regulate such hydride transfers and reductions. Further understanding of these factors should permit enhanced control of chemoselectivity of reductions. We are currently pursuing studies to elucidate the role of hydridoborate structure in hydride transfers.

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(11) (a) Brown, C. A. 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 29–Sept 3, 1976; American Chemical Society: Washington, D.C., 1976; Abstr. ORGN 153. (b) Similar results are obtained with triethylborane. Spectra of solutions of triethylhydridoborate are extremely sensitive to traces of free triethylborane.[1e,11a,c] (c) Brown, H. C.; Khuri, A.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1977**, *99*, 6237–6242.
(12) Potassium triisopropoxyhydridoborate in THF shows little or no reaction at ambient temperature with most organic functionality other than ketones and aldehydes. Even alcohols and carboxylic acids liberate hydrogen exceptionally slowly compared with other group 3 hydrides.[1b,4]
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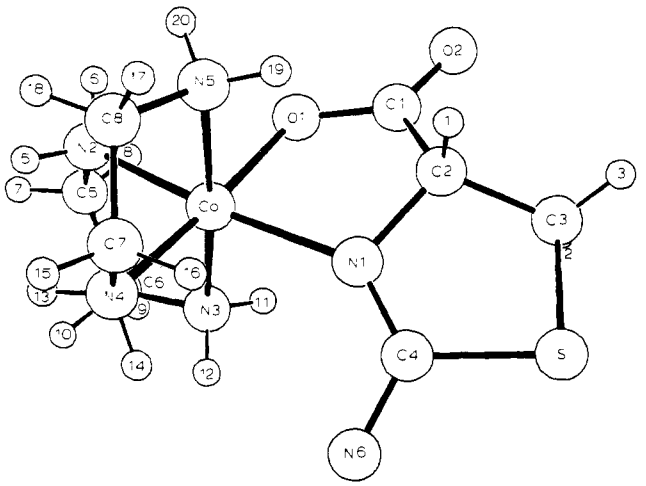


Figure 1. The structure of Δ-[bis(ethylenediamine)-(*R*)-2-aminothiazoline-4-carboxylatocobalt]$^{2+}$. Relevant bond lengths: Co–N(1), 1.96 (1); N(1)–C(4), 1.29 (2); C(4)–N(6), 1.32 (3); S–C(4), 1.76 (3); S–C(3), 1.83 (3); C(2)–N(1), 1.49 (2); mean Co–N, 1.96 Å. Crystal data: $CoCl_2SO_{10}N_6C_8H_{21}$;[4] monoclinic; a = 17.325 (14), b = 14.194 (11), c = 8.295 (8) Å; β = 102.82 (2)°; space group $C2$; M = 523.2 daltons; d_m = 1.77 (±0.02), d_c = 1.75 g cm^{-3}; Z = 4, μ = 13.3 cm^{-1} (Mo Kα). For the 1150 independent reflections collected with a Hilger and Watts four-circle diffractometer with $F_o^2 > 3\sigma(F_o^2)$, the R index is 0.069.

Synthesis and Structure of a 2-Aminothiazolinecobalt(III) Complex Derived from (*R*)-Cysteine

Sir:

The remarkable oxidation-condensation reaction of Δ-[Co(en)$_2$-(*R*)-cysteinato](ClO$_4$)$_2$ (I) to give the sulfenamide product II in a dimethyl sulfoxide-acetic anhydride mixture was described recently.[1] The sulfur in II is very susceptible to both electrophilic and nucleophilic attack and we have reported some nucleophilic reactions of II with $S_2O_4^{2-}$, BH_4^-, and mercaptide ions.[2,3] The CN^- ion also reacts with II in a complex manner herein described.

The Δ-sulfenamide II and aqueous NaCN (1–2 equiv) reacted within the time of mixing (20 °C) to give a deep-red-burgundy-colored solution which on acidification (HClO$_4$) deposited crystals with the stoichiometry [Co(C$_2$H$_8$N$_2$)$_2$-(C$_4$H$_5$N$_2$SO$_2$)](ClO$_4$)$_2$.

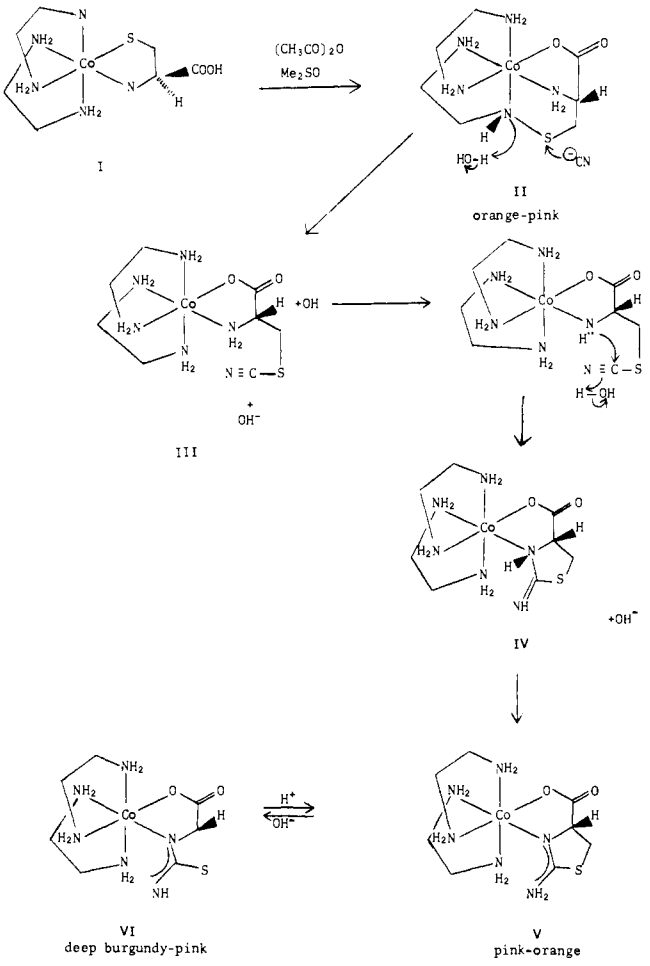
The visible spectrum for this product (0.01 M HClO$_4$) showed two ligand field bands (ϵ_{max}^{497} 163, ϵ_{sh}^{350} 198 M^{-1} cm^{-1}; $[M]_{436}^{20}$ +7750 deg M^{-1} m^{-1}) indicative of the Co^{III}N$_5$O chromophore. Also the spectrum implies detachment of the sulfur from the Co–N–S moiety of the reactant sulfenamide which has its second ligand field band obscured by the intense charge-transfer absorption associated with the Co–NH(*R*)–S: group.

The ^{13}C and ^{1}H NMR spectra and chromatography of the product indicated the formation of a single isomer, while the rotatory dispersion spectrum (10^{-2} M HClO$_4$) suggested the same absolute configuration about cobalt as the starting material (Δ), on comparison with reference spectra of several Λ and Δ (Co(en)$_2$(amino acido)]$^{n+}$ complexes.[5] A similar but chemically distinct product was obtained also from the diastereoisomeric Λ-sulfenamide and CN^-.

These results suggested that the CN^- reaction involved neither attack at, nor mutarotation about, cobalt. The data did not allow, however, a conclusive structural assignment and therefore an X-ray crystallographic study was undertaken on the perchlorate salt derived from the Δ-sulfenamide.[4]

The structure (Figure 1) consists of independent divalent cations and ClO_4^- ions linked by H bonds. It indicates that CN^- has attacked the sulfur center and cleaved the sulfenamide linkage. The dangling thiocyanate III so formed is then attacked by the deprotonated amine group of the amino acid chelate to generate finally an unusual amino acid chelate, the 2-aminothiazoline-4(*R*)-carboxylato ion, bound through a N atom of the thiaamidine moiety. Overall the six-membered sulfenamide ring has opened and a new five-membered thi-

Scheme I



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