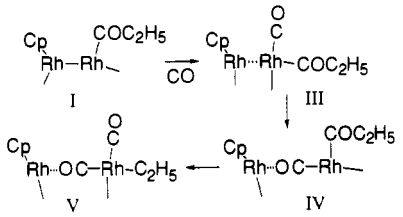
Scheme II



calculated stabilities for all the steps exclude steric and strain instabilities expected on the actual surface.

In place of Scheme I we propose Scheme II. Here CO binds to the acylated Rh fragment on the right to form III. However, the Rh-Rh bond in III is broken so it rearranges to IV with CO nearly colinear with the Rh-Rh axis. Species IV rearranges to V which, like species II that was proposed in ref 2 for Scheme I, has two CO bound to the right-hand Rh, but one of them binds weakly through O to the left-hand Rh. The Rh-Rh distance in II is large, which is consistent with the EXAFS result, and the CO IR spectrum will show splitting as seen in ref 3. The activation energy for the CO insertion reaction, going from V to IV, and its reverse, has not been calculated but, based on a theoretical study involving another low-coordinate transition metal cation,[11] it should be small.

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Notes

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A New and Convenient Synthesis of Sodium Carboxylatotrihydroborate, $Na_2BH_3CO_2$, a Boron Analogue of Sodium Acetate

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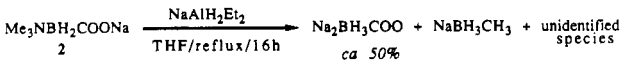
Acetate ion is a simple yet important species involved in several biological processes,[1] including the biosynthesis of cholesterol. An isoelectronic and isostructural boron analogue of acetate ion is the carboxylatotrihydroborate anion, $H_3BCO_2^{2-}$ (**1**). Thus, **1** may have interesting biological properties due to its structural similarities to the acetate ion. **1** is also isoelectronic with the carbonate ion and is commonly called boranocarbonate.[2] Malone and Parry,[2] while comparing the chemical properties of isoelectronic BH_3CO and CO_2, synthesized several salts of **1** by reaction of H_3BCO with alcoholic base. They also showed that H_3BCO can be regenerated from salts of **1** by reaction with 85% H_3PO_4. Use of H_3BCO as an acyl ion equivalent has been demonstrated previously,[3,4] and provides a convenient route for incorporating boron into molecules with easy to acylate functionalities. The resulting species may have potential in boron neutron capture therapy (BNCT). Since salts of **1** are stable for long periods under ambient conditions, these should be convenient solid storage sources for the generation of BH_3CO upon demand. In addition, they may also be of value as selective reducing agents[4] (such as found for cyanoborohydride).

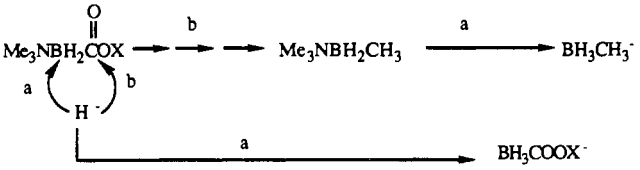
Despite the potential use of **1**, studies of the chemistry and biological activity of this species have been limited due in part to the hazardous nature of its synthesis. The previous synthesis,[2] as mentioned (vide supra), involved the use of H_3BCO, which itself is prepared from B_2H_6 and CO under pressure. Not only are all these gases hazardous, but the synthesis also requires use of special equipment. We now wish to report a new and convenient synthesis of sodium boranocarbonate and the results of preliminary studies of its biological activity.

Reaction of the sodium salt[5] of trimethylamine-carboxyborane[6] (**2**) with 2 molar equiv of sodium diethyldihydroaluminate (Aldrich) in refluxing THF yielded **1** in ca. 50% yield[7] according to Scheme I. The product was easily isolated by filtration under an inert atmosphere. The major byproduct was the completely

Scheme I



Scheme II



reduced species $NaBH_3CH_3$, which stayed in solution with small amounts of other unknown byproducts. At least 1.5 molar equiv of reagent was necessary to completely consume the starting material under the conditions reported. With lower amounts of reagent (1.0-1.25 equiv), a small amount of unreacted starting material contaminated the product without increasing the yield (by decreasing the amount of reduction). Free trimethylamine-carboxyborane could also be used as substrate, but it consumed extra valuable reagent by immediate conversion to salt.

Attempts to prepare *O*-methylboranocarbonate, $H_3BC(O)OMe^-$, from trimethylamine-carbomethoxyborane,[8] $Me_3NBH_2CO_2Me$, by a similar procedure were unsuccessful; instead formation of $BH_3CH_3^-$ was observed. Reaction[9] of Me_3NBH_2COOX (X = H, Na, Me) with several other hydrides (except NaH) either gave no reaction or formed $M^+BH_3CH_3^-$ and/or $Me_3NBH_2CH_3$ (Table I). This itself is a new method for the preparation of $M^+BH_3CH_3^-$ and has been utilized for the

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(5) **2** was prepared in 97% yield by reaction of Me_3NBH_2COOH with $NaHCO_3$ using a procedure similar to the one reported by Morse et al. (Norwood, V. M., III; Morse, K. W. *Inorg. Chem.* **1986**, *25*, 3690-3693). ^1H NMR: 2.60 ppm, s. ^{11}B NMR: -8.00 ppm, t, $^1J_{B,H}$ = 94 ● 1 Hz.
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(7) Yields up to 66% have been obtained. ^1H NMR: 0.73 ppm, q, $^1J_{^{11}B,H}$ = 80 ± 1 Hz, and septet, $^1J_{^{10}B,H}$ = 26.7 ± 0.21 Hz. ^{11}B NMR: -31.1 ppm, q, $^1J_{^{11}B,H}$ = 80 ± 2 Hz. Anal. Calcd for $BH_3CO_2Na_2$: C, 11.57; H, 2.91; B, 10.41. Found: C, 11.26; H, 2.92; B, 9.79.
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(9) The reactions were followed by ^{11}B NMR spectroscopy.

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Table I. Reaction of Me_3NBH_2COOX (X = H, Na, Me) with Various Hydrides

hydride	no. of molar equiv	conditions	results
		X = Me	
Et_4NBH_4[11]	2	CH_2Cl_2/reflux/64 h	no reaction[a]
$NaBH_4$	4	diglyme/reflux/60 h	no reaction[b]
$NaBH_4$/MeOH[12]	2.5	diglyme/reflux/1 h[c]	no reaction[a]
K-Selectride ($KB[CH(CH_3)C_2H_5]_3H$)	2	THF/rt/72 h	trace amount of $Me_3NBH_2CH_3$[d] remaining unreacted[b]
		reflux/16 h	same results
$LiAl(O\text{-}^tBu)_3H$	2	THF/reflux/24 h	small amount of $Me_3NBH_2CH_3$[d] remaining unreacted
$NaAlH_2Et_2$	2	Et_2O/rt/24 h	$NaBH_3CH_3$
$LiAlH_4$	1 or 2	Et_2O/rt/1 h	$LiBH_3CH_3$ + trace $Me_3NBH_2CH_3$
		X = H	
$NaBH_4$	2	THF/reflux/1.5 h	Me_3NBH_3[b,e]
$LiAlH_4$	2	Et_2O/rt/1 h	$LiBH_3CH_3$, some $Me_3NBH_2CH_3$
	1	Et_2O/-78 °C/6 h	$LiBH_3CH_3$, Me_3NBH_2COOLi
$LiAl(O\text{-}^tBu)_3H$	2	THF/reflux/72 h	Me_3NBH_2COOLi
		X = Na	
$NaBH_4$	2	THF/reflux/4 h	no reaction[b]
NaH	2	THF/reflux/48 h	decomposition to species without B-H bonds, small amount of Na_2BH_3COO and unreacted starting material
Vitride	2	THF/reflux/19 h	MBH_3CH_3
$LiAlH_4$	2	THF/rt/24 h	MBH_3CH_3

[a] Hydride reagent completely decomposed. [b] Some decomposition of hydride reagent. [c] The reaction mixture was refluxed for 1 h prior to addition of MeOH and then refluxed for another 1 h. [d] Since $Me_3NBH_2CH_3$ is very volatile, some of it may have escaped during the reaction. [e] Me_3NBH_3 is probably formed by the displacement reaction of diborane (generated as follows: $Me_3NBH_2COOH + NaBH_4 \rightarrow Me_3NBH_2COONa + H_2 + {}^1/_2B_2H_6$) with $Me_3NBH_2COOH(Na)$. Since no Na_2BH_3COO was observed, the displacement product, $BH_2COOH(Na)$, must degrade quickly before it can convert to **1**.

preparation of $Me_3NBH_2CH_3$ and subsequently $NH_3BH(CH_3)$-$CONHEt$,[10] the amide of the boron analogue of alanine (the first boron analogue of amino acids with a side chain). With NaH as the hydride source and X = Na, formation of small amounts of **1** was observed along with major decomposition.

Formation of **1**, MBH_3CH_3, and in some cases $Me_3NBH_2CH_3$ depends upon the rate of the following two reactions: (a) displacement of Me_3N by H^-; (b) reduction of the carbonyl group (Scheme II). In the case where X = Me (and reduction is observed), the reduction of carbonyl is much faster than displacement of Me_3N. Thus, formation of only $Me_3NBH_2CH_3$ (in small amounts) is observed upon reduction with K-Selectride ($KB[CH(CH_3)C_2H_5]_3H$ or LiAl ($O\text{-}^tBu)_3H$. With stronger hydride reagents, reaction b is followed by reaction a.

The carbonyl group in **2** is quite difficult to reduce, and when $NaAlH_2Et_2$ is used as the hydride source, both reactions proceed at a similar rate. The carbonyl group of **1**, formed by displacement of Me_3N from **2**, is even harder to reduce not only because of the negative charges on the adjacent atoms but also due to the insolubility of **1** in THF. From the data presented in Table I, it is also clear that the partially reduced species are very susceptible to reduction and are probably reduced as soon as they are formed.

In summary, a convenient synthesis of sodium boranocarbonate is described. Not only does it easily make available large amounts of **1** for biological studies and for selective reduction studies, but it also provides an easy source of BH_3CO for incorporation of boron into potential BNCT agents.

In pharmacological studies[13] in murine model screens, compound **1** has shown significant hypocholesterolemic[14] and anti-inflammatory[15] activity. These data will be published separately.

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Registry No. Na_2(**1**), 17363-08-5; **2**, 103904-11-6; $NaAlH_2Et_2$, 17836-88-3; $Me_3NBH_2CH_3$, 52920-77-1; $NaBH_3CH_3$, 141344-69-6; $LiBH_3CH_3$, 52950-75-1; Me_3NBH_3, 75-22-9; $LiBH_3CH_3$, 52950-75-1; Me_3NBH_2COOLi, 141344-70-9; Me_3NBH_2COOMe, 91993-52-1; Me_3NBH_2COOH, 60788-33-2; Et_4NBH_4, 17083-85-1; $NaBH_4$, 16940-66-2; $KB[CH(CH_3)C_2H_5]_3H$, 54575-49-4; $LiAl(O\text{-}^tBu)_3H$, 17476-04-9; $LiAlH_4$, 16853-85-3; vitride, 22722-98-1.

Supplementary Material Available: Text giving a detailed synthesis of sodium carboxylatotrihydroborate (1 page). Ordering information is given on any current masthead page.

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Oxidation State of Platinum in Oxidative-Addition Reactions and η^1-I_2 Products from Dihalogen Reactions with Organoplatinum(II) Complexes, As Inferred from Monochromatic X-ray Photoelectron Spectroscopy

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Introduction

Continuing our investigations of oxidative-addition reactions, we have studied in detail the reactions of dihalogens, alkyl halides, and organotin(IV) complexes with various Pt(II) complexes containing the terdentate monoanionic ligand [C_6H_3-

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