proximately equal to k, and k_c slightly different from $k_{c'} \approx k_i$, i.e., consistent with the C_s symmetry of the carbonyl species (see Figure 3). The results of this calculation are found in Table I along with the CO stretching force field. As noted in Table I, the CO stretching force constant trans to the hydride (k_1) is slightly greater than that which is trans to the phosphine ligand (k_2) as would be anticipated.

The degree to which oxygen-18 has been incorporated into the $\mathrm{HMn(CO)_3[diphos]}$ species is considerably less than that in the corresponding $[\mathrm{Mn(CO)_4(diphos)}]^+$ precursor at high amine concentration. This observation would of course be anticipated since both processes, oxygen exchange and metal hydride production, are occurring at comparable rates and the once formed $\mathrm{HMn(CO)_3[diphos]}$ derivative has been demonstrated not to exchange oxygen atoms with $\mathrm{H_2{}^{18}O}$ directly. Contrasting the extent of oxygen-18 incorporation into the parent $[\mathrm{Mn(CO)_4(diphos)}]^+$ species vs. that in the $\mathrm{HMn(CO)_2[diphos]}$ (i.e., comparing Figures 1B and 2), it is quite obvious that the intermediate common to both processes is proceeding to hydride to a greater degree as the concentration of base is increased (eq 5, where rate$_2$ is enhanced by the presence of base). For the various concentrations of added

$$[\mathrm{MnCO}]^+ + {}^{18}\mathrm{OH}^- \rightarrow [\mathrm{MnCO^{18}OH}] \xrightarrow{\text{rate}_1} [\mathrm{MnC^{18}O}]$$

$$\xrightarrow{\text{rate}_2} [\mathrm{MnH}] + \mathrm{C^{16}O^{18}O} \quad (5)$$

triethylamine there was a dependence on the relative rates of oxygen-18 incorporation of about $[\mathrm{Et_3N}]^{1/2}$ as would be expected for ${}^-\mathrm{OH}$ catalysis (i.e., $\mathrm{Et_3N + H_2O \rightleftharpoons Et_3NH^+ + {}^-OH}$). On the other hand, there was observed a greater dependence of the relative rates of hydride production on the initial triethylamine concentration.

These observations have previously been ascribed to a deprotonation of the hydroxycarbonyl intermediate by base followed by hydrolysis of the reduced metal species produced via loss of $\mathrm{CO_2}$, in this case $[\mathrm{Mn(CO)_3(diphos)}]^-$ (eq 6).[3]

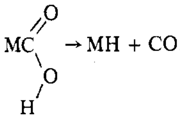
$$\begin{tikzcd}
{[\mathrm{Mn(COOH)}] + {}^-\mathrm{OH(Et_3N)} \rightleftharpoons [\mathrm{MnCOO}]^- + \mathrm{H_2O(Et_3NH^+)}} \arrow[d] \\
{[\mathrm{Mn}]^- + \mathrm{CO_2}} \arrow[d, "\mathrm{H_2O}"'] \\
{[\mathrm{MnH}] + {}^-\mathrm{OH}}
\end{tikzcd} \quad (6)$$

Other reductive processes where the $\mathrm{MCO_2H}$ group has been postulated as an intermediate have appeared in the literature,[11-13] including the $[\mathrm{HgCO_2H}]^+$ moiety in the reduction of Hg(II) to Hg(0) by carbon monoxide.[12] Similarly, a complex containing the closely related $[\mathrm{MCONHCH_3}]$ grouping has been found to react with base to afford the reduced metal species (eq 7).[14]

$$\mathrm{(C_5H_5)W(CO)_3C(O)NHCH_3 + Et_3N} \rightarrow$$

$$\mathrm{(C_5H_5)W(CO)_3{}^- + CH_3N{=}C{=}O + Et_3NH^+} \quad (7)$$

Nonetheless, there are probably two mechanisms operative in [MH] formation via $\mathrm{CO_2}$ elimination from the [MCOOH] intermediates; these being a concerted β-H migration (eq 8)



$$\mathrm{MC(=O)OH} \rightarrow \mathrm{MH + CO_2} \quad (8)$$

which usually requires a vacant site on the metal or the base-catalyzed reductive process (eq 6). Indeed pyrolysis of the only stable example of a metal complex containing the hydroxycarbonyl ligand, $[\mathrm{IrCl_2(CO_2H)(CO)L_2}]$ ($\mathrm{L = Me_2PhP}$ or $\mathrm{Me_2PhAs}$), in the solid state affords the corresponding IrH complex plus carbon dioxide.[15]

In conclusion, it is apparent from the studies reported here that in order to influence the rate of MH formation from the reaction of KOH with metal carbonyl derivatives where this step is reluctant, it would be advantageous to use excess quantities of KOH even though the reaction may be catalytic in hydroxide ion (e.g., eq 9).[16] This process is indeed highly

$$\begin{tikzcd}
{\mathrm{Cr(CO)_6} + {}^-\mathrm{OH}} & \rightleftharpoons & {[\mathrm{Cr(CO)_5COOH}]^-} \arrow[d] \\
{[\mathrm{Cr(CO)_5H_2}] + {}^-\mathrm{OH}} \arrow[u, "\text{excess CO}", "-\mathrm{H_2}"'] & & {\mathrm{Cr(CO)_5H^-} + \mathrm{CO_2}} \arrow[ll, "\mathrm{H_2O}"']
\end{tikzcd} \quad (9)$$

desirable in the homogeneous catalyzed water–gas shift reaction by metal carbonyl derivatives. On the other hand if it is desirable to enrich the metal carbonyl derivative with oxygen-18 or oxygen-17 it is preferable to carry out the reaction in a minimum of hydroxide ion.[17] However, in cases where metal hydride formation is quite rapid relative to the reverse process involving loss of ${}^-\mathrm{OH}$ from the hydroxycarbonyl intermediate (e.g., the reaction of $\mathrm{Ru_3(CO)_{12}}$ with $\mathrm{OH^-}$)[16-19] large concentrations of ${}^-\mathrm{OH}$ should be much less important for production of metal hydride species.

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Registry No. **1**, 36352-75-7; **2**, 67530-47-6; **3**, 67576-70-9; **4**, 67530-48-7; **5**, 67597-59-5; **6**, 67530-49-8; $[\mathrm{Mn(CO)_4(diphos)}](\mathrm{PF_6})$, 6443-17-0; $\mathrm{H_2{}^{18}O}$, 14314-42-2.

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Reaction of Trimethylamine–Fluoroboranes with Phosphine and Amine Bases

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Reactions where two donor molecules compete for one acceptor have been used to compare the preferences of ac-

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Table I. Equilibrium Yields[a] of Trimethylamine and Equilibrium Constants[b] in Displacement Reactions

	$(CH_3)_3P$		$(C_6H_5)_3P$		$(CH_3)_2NH$		CH_3NH_2	
borane	% $(CH_3)_3N$	K[b]	% $(CH_3)_3N$	K	% $(CH_3)_3N$	K	% $(CH_3)_3N$	K
BH_3	79[c]	14.2	8.4 ± 1.0	8.4×10^{-3}	56 ± 2	1.6	46 ± 1	0.73
BH_2F	29 ± 3[d]	0.17	1.5 ± 0.5	2.3×10^{-4}	63 ± 1[e]	2.9	84 ± 1[e]	27.6
BHF_2	24 ± 3	0.10	0.9 ± 0.3	8.3×10^{-5}	75 ± 2	9.0	85 ± 1	32.1
BF_3	19[c]	0.06	0.5 ± 0.3	2.5×10^{-5}	78 ± 4	12.5	98 ± 1	2401

[a] In mol %. [b] Equilibrium constant calculated for displacement reactions written as $(CH_3)_3NBH_nF_{3-n}$ + base → base$\cdot BH_nF_{3-n} + (CH_3)_3N$. [c] Results from only one run confirming previously published values.[2] [d] Average of two or three runs for each reaction. [e] ^{11}B NMR showed disproprotionation of BH_2F giving BH_3 and BF_3 adducts.

ceptors for various types of donors.[1-3] In the competition reaction shown in eq 1, trimethylamine and trimethyl-

$$(CH_3)_3N\cdot BH_3 + (CH_3)_3P \rightleftarrows (CH_3)_3P\cdot BH_3 + (CH_3)_3N \quad (1)$$

phosphine, in effect, compete for 1 equiv of borane.[1,2] At equilibrium, 80 ± 3% of the borane was found as the trimethylphosphine adduct, illustrating the preference of borane for the phosphine donor over the amine donor. Although the equilibrium constant in such reactions is controlled by the usual thermodynamic parameters, useful insights have been gained by the application of the HSAB model.[4] Borane, which is classified as a soft acid, shows a preference in this reaction for the softer phosphine base over the harder amine base in concert with the HSAB model. Trifluoroborane, under analogous circumstances (eq 2), was found essentially 100%

$$(CH_3)_3N\cdot BF_3 + (CH_3)_3P \rightleftarrows (CH_3)_3P\cdot BF_3 + (CH_3)_3N \quad (2)$$

as the trimethylamine adduct, demonstrating the preference of the hard acid,[4] BF_3, for the harder base. Very similar results were obtained from direct solid–gas reactions at elevated temperatures[1] and from reactions in organic solvents,[2] provided that sufficient time was allowed for the establishment of equilibrium.

We have used base-displacement reactions to investigate the acceptor characteristics of BH_2F and BHF_2 toward selected nitrogen and phosphorus donors. Our earlier attempts[5] to prepare the free fluoroboranes via acid-displacement reactions gave only the disproportionation products B_2H_6 and BF_3, so calorimetric measurements of direct fluoroborane–adduct formation have not been feasible. Nevertheless, it was felt that even the qualitative comparisons of adduct stabilities afforded by homogeneous base-displacement reactions would help elucidate how fluorine affects the acceptor strength of fluoroboranes.

A modification of the procedure of Young, McAchran, and Shore[2] was used in our reactions of trimethylamine–fluoroboranes with $(CH_3)_3P$, $(C_6H_5)_3P$, $(CH_3)_2NH$, and CH_3NH_2. A measured quantity (5–10 mmol) of the trimethylamine–borane or –fluoroborane adduct was placed in a dry flask fitted with a vacuum adapter and a magnetic stirbar. The flask was then attached to the vacuum line and evacuated, and an equimolar quantity of displacing base condensed into the vessel. (In the case of triphenylphosphine the two solids were added simultaneously.) Then 7.0 mL of dry benzene was condensed into the flask, the Teflon valve was closed, and the contents were permitted to warm to room temperature and stir for 48 h. This time interval was chosen after periodically determining the progress of several trial reactions by fractionating the reaction mixture volatiles through traps held at –78, –96, and –196 °C, measuring the free trimethylamine (–196 °C trap), and condensing all volatiles back into the reaction vessel for further reaction. Where possible, the reactions were also monitored by ^{1}H NMR for completeness. In no case tested were changes noted after about 12 h. We were unable to confirm the equilibrium positions by carrying out reverse reactions because the necessary phosphine– and amine–fluoroboranes have not been isolated and characterized.

In a typical reaction 0.6427 g (6.85 mmol) of $(CH_3)_3N\cdot BH_2F$[6] was combined with 6.86 mmol of $(CH_3)_3P$ and 7.0 mL of C_6H_6. After 48 h of stirring at room temperature, 1.99 mmol (29%) of $(CH_3)_3N$ was obtained by fractionation.[7] The equilibrium quantities of free $(CH_3)_3N$ and the corresponding equilibrium constants for the four amine- and phosphine-displacing bases are shown in Table I.

The difficulty in quantitative fractionation of the methylamines led us to determine the $(CH_3)_3N$ yields in $(CH_3)_2NH$ and CH_3NH_2 displacements by integration of ^{1}H and ^{11}B resonance signals of the products in the equilibrium mixture and by careful measurement of the apparent gas-phase molecular weight of the binary amine mixtures, which permitted calculation of the amount of $(CH_3)_3N$ present. Whenever possible, both methods were used and excellent agreement was found between the results.

The product mixtures from the BH_2F and BHF_2 adduct reactions were intractable and we were unable to isolate pure products, although, in several cases ^{1}H and ^{11}B NMR spectra were observed. We have reported[8,9] the use of this method for synthesis of new fluoroborane adducts of the strong bases aza- and diazabicyclooctane.

It is noteworthy that monofluoroborane adducts of methyl- and dimethylamine were observed to disproportionate during the displacement reactions giving BH_3 and BF_3 adducts. While the mechanism of this apparent disproportionation is not clear, its presence means that the equilibrium yields of trimethylamine from those reactions are probably not directly comparable with the other values.

The results from the trimethylphosphine reactions (Table I) indicate that incorporation of fluorine in the borane group substantially increases its hardness as evidenced by the marked decrease in trimethylamine yield and the equilibrium constant between the BH_3 and BH_2F adducts. This difference is in accord with the expected effect, according to the HSAB model, of the fluorine on the polarizability and related properties of the borane group. In spite of this change, the B–N distance in $(CH_3)_3N\cdot BH_2F$ is not significantly different from that in $(CH_3)_3N\cdot BH_3$.[11]

Addition of the second and third fluorines produces similar but much smaller increases in the apparent hardness of the fluoroborane moiety as judged by their increasing preference for N donors over P donors.

An analogous trend is seen in Table I for the triphenylphosphine reactions. The smaller overall magnitude of the equilibrium constants and percent $(CH_3)_3N$ evolved in these reactions indicate that triphenylphosphine is a weaker donor toward boranes than is trimethylphosphine. The similarity in the order of percent $(CH_3)_3N$-evolved values in the reactions of the two bases suggests that the different organic groups do not appreciably affect the soft character of the phosphorus donor site.

Pearson[12] lists ammonia and primary amines as hard bases and suggests that methyl groups exert an electron-withdrawing inductive effect (in the absence of unsaturated groups), from which one might conclude that CH_3NH_2, $(CH_3)_2NH$, and

$(CH_3)_3N$ should be progressively harder bases than ammonia. If preference for BF_3 over BH_3 is taken as a measure of hardness, our results indicate that both CH_3NH_2 and $(CH_3)_2NH$ are hard bases since both produce larger equilibrium constants with BF_3 than with BH_3. However, methylamine shows a greater preference for the hard fluoroborane acceptors than does dimethylamine, while a slight reverse preference is observed for the soft borane acceptor. These observations suggest that methylamine behaves as a harder base than dimethylamine in this system. Only a qualitative comparison is justified, however, in view of the relatively small differences observed and the numerous factors which can affect the equilibrium constants.

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Registry No. $(CH_3)_3N\cdot BH_3$, 75-22-9; $(CH_3)_3N\cdot BH_2F$, 35449-24-2; $(CH_3)_3N\cdot BHF_2$, 35237-72-0; $(CH_3)_3N\cdot BF_3$, 420-20-2; $(CH_3)_3P\cdot BH_3$, 1898-77-7; $(CH_3)_3P\cdot BH_2F$, 67226-44-2; $(CH_3)_3P\cdot BHF_2$, 67194-37-0; $(CH_3)_3P\cdot BF_3$, 420-21-3; $(C_6H_5)_3P\cdot BH_3$, 2049-55-0; $(C_6H_5)_3P\cdot BH_2F$, 67194-38-1; $(C_6H_5)_3P\cdot BHF_2$, 67194-39-2; $(C_6H_5)_3P\cdot BF_3$, 850-07-7; $(CH_3)_2NH\cdot BH_3$, 74-94-2; $(CH_3)_2NH\cdot BH_2F$, 67194-40-5; $(CH_3)_2NH\cdot BHF_2$, 42525-42-8; $(CH_3)_2NH\cdot BF_3$, 811-59-6; $CH_3NH_2\cdot BH_3$, 1722-33-4; $CH_3NH_2\cdot BH_2F$, 67194-41-6; $CH_3NH_2\cdot BHF_2$, 42525-40-6; $CH_3NH_2\cdot BF_3$, 373-56-8.

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Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 13. Acid-Catalyzed Aquation of ($\alpha\beta S$)-Carbonato(tetraethylenepentamine)cobalt(III) Ion and Carbon Dioxide Uptake by ($\alpha\beta S$)-Aquo(tetraethylenepentamine)cobalt(III) Ion[1]

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Previous studies in this series dealing with complexes of the pentaammine type have embraced the acid-catalyzed decarboxylation kinetics of the species $M(NH_3)_5(CO_3)^+$ ($M \equiv$ Co(III),[2] Rh(III),[3] and Ir(III)[3]) and the carbon dioxide uptake kinetics[4] of $Co(NH_3)_5(OH)^{2+}$. Other studies have dealt with the acid-catalyzed carbonato ring-opening and decarboxylation reactions of various chelated carbonato complex ions of the general type $Co(N)_4(CO_3)^+$, where $(N)_4$ represents a tetrafunctional grouping of amine ligands. Large variations have been noted in the rate of the ring-opening process, depending on the nature of the "nonparticipating" tetraamine grouping.[5,6] While no ring opening is involved in the acidic hydrolysis of carbonatopentaamine complexes, it was of interest to us to examine the effect of a drastic change in the pentaamine grouping on both the decarboxylation process and on its reverse, the carbon dioxide uptake by the corresponding aquopentaamine species. As our first study of this nature, we have examined the reactions of the carbonato cobaltic complexes containing the straight-chain pentadentate species tetraethylenepentamine.

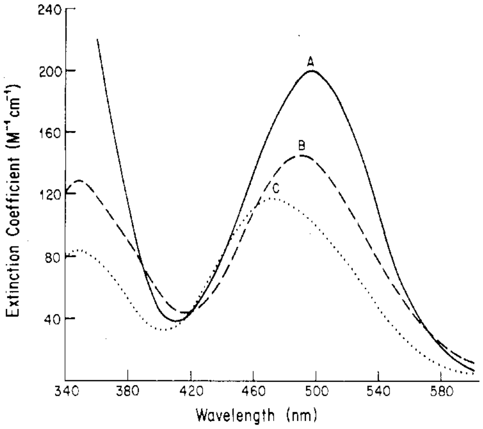

Figure 1. UV–visible spectra of some (tetraethylenepentamine)cobalt(III) complexes: (A) $\alpha\beta S$-$[Co(tetren)(CO_3)]ClO_4$; (B) $\alpha\beta S$-$[Co(tetren)(OH)](ClO_4)_2$; (C) $\alpha\beta S$-$[Co(tetren)(OH_2)](ClO_4)_3$.

Experimental Section

Materials. Tetraethylenepentamine(tetren) was used as obtained from Matheson Coleman and Bell. All other chemicals were of reagent grade. Deionized and degassed water was used in preparing all solutions.

Preparation and Characterization. ($\alpha\beta S$)-Hydroxo- and ($\alpha\beta S$)-aquo(tetraethylenepentamine)cobalt(III) perchlorates were prepared and characterized as described by House and Garner.[7-9] ($\alpha\beta S$)-Carbonato(tetraethylenepentamine)cobalt(III) perchlorate was prepared as follows. Solid Li_2CO_3 is slowly added to a stirred solution containing 2 g of $[Co(tetren)(OH)](ClO_4)_2$ in a minimum amount of water until a pH of 8–8.5 is attained. The solution is stirred for 5 min and cooled in an ice bath, and an equal volume of absolute ethanol is added. The mixture is allowed to stand for a few minutes in the ice bath, filtered, and washed thoroughly with ethanol. The filtrate is then evaporated to dryness. Bright red platelike crystals are obtained. Anal. Calcd for $[Co(tetren)(CO_3)](ClO_4)\cdot 3H_2O$: C, 23.40; H, 6.29; N, 15.18. Found:[10] C, 23.56; H, 6.16; N, 15.28.

Spectra. The absorption spectra in the UV–visible region were obtained by use of a Cary 15 spectrophotometer. The spectrum of the carbonato complex was determined in dilute sodium bicarbonate solution to avoid hydrolysis and is very similar to that of the $Co(NH_3)_5CO_3^+$ complex ion. (A steep charge-transfer absorbance increase near 350 nm for both complexes is diagnostic of the presence of monodentate carbonato ligand.) After treatment with acid, the carbonato complex solution gave a spectrum identical with that of $\alpha\beta S$-$Co(tetren)(OH_2)^{3+}$, confirming that the geometry of the carbonato species is $\alpha\beta S$. The electronic spectra of aquo, hydroxo, and carbonato complexes are presented in Figure 1. The infrared spectrum of the carbonato complex was measured on a Beckman IR5A spectrometer using the KBr disk technique and exhibits two CO stretching frequencies at 1458 and 1340 cm^{-1} to be compared with 1453 and 1373 cm^{-1} for the $Co(NH_3)_5CO_3^+$ complex ion.[11]

Kinetic Runs. The kinetics of acid-catalyzed aquation of the carbonato species were studied between 15 and 30 °C at an ionic strength of 0.5 M (NaCl) and over an acidity range of $1 \le pH \le$

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