Carbon monoxide-borane adducts with tertiary amines

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Carbon Monoxide–Borane Adducts with Tertiary Amines

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Contribution from the Department of Chemistry, the University of Pittsburgh, Pittsburgh, Pennsylvania 15260. Received February 16, 1973

Abstract: The reaction of carbon monoxide–borane with tertiary amines has been studied. Trimethylamine yields a 1:1 adduct stable at low temperatures. Its structure has been assigned as $H_3BC(O)N(CH_3)_3$. Thermal dissociation of $H_3BC(O)N(CH_3)_3$ yields initially carbon monoxide–borane and trimethylamine. At higher temperatures these materials react by base displacement to yield carbon monoxide and trimethylamine–borane. Triethylamine and triphenylphosphine also add to carbon monoxide–borane, but pyridine does not. Low temperature infrared spectral data are given for $H_3BC(O)N(CH_3)_3$ over the range 3000–300 cm^{-1}. Boron-11 nmr data are given for H_3BCO and $H_3BCO \cdot N(CH_3)_3$.

The reaction of carbon monoxide–borane with ammonia and trimethylamine was first reported by Burg and Schlesinger.[1] These workers reported that carbon monoxide–borane and trimethylamine do not react at −78° but yield carbon monoxide and trimethylamine–borane by base displacement at 25°. Reaction of carbon monoxide–borane with ammonia did not yield carbon monoxide but at low temperatures formed a stable adduct containing two molecules of ammonia to one carbon monoxide–borane. The structure of the ammonia adduct has been established by Carter and Parry[2] as ammonium boranocarbamate, $[NH_4^+][H_3BC(O)NH_2^-]$. Only traces of the base displacement product, ammonia–borane, were observed. Carter and Parry also found that methylamine and dimethylamine react in the same fashion as ammonia, yielding analogous boranocarbamate derivatives. Evidence was obtained for a low temperature reaction between trimethylamine and carbon monoxide–borane in ethers, but the carbamate type derivative was not found. The present study establishes the structure of $(CH_3)_3N \cdot OCBH_3$.

Results and Discussion

Carbon monoxide–borane reacts with trimethylamine, either neat or in methyl ether at −126 to −111°, to form a 1:1 adduct. The adduct is a white solid at −65° which dissociates into the starting materials at −45° or above. The adduct sublimes readily under high vacuum at −63° but appears to be completely dissociated in the gas phase on the basis of vapor-phase molecular weight measurements. When weighed samples were warmed rapidly in a calibrated volume, the pressure reached a maximum which gave a calculated molecular weight of 51.1 (expected for $H_3BCO \cdot N(CH_3)_3$ = 101.0). On standing for several seconds, crystals of trimethylamine–borane formed, and the pressure dropped to half the maximum value measured. This pressure was entirely from carbon monoxide liberated by the base displacement reaction. The molecular weight obtained by rapid pressure measurement is, within experimental error, half that expected for the adduct and is the average of the molecular weights of the two components, trimethylamine and carbon monoxide–borane, present in equal molar amounts. This relatively slow formation of $(CH_3)_3NBH_3$ allows

(1) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **59**, 780 (1937).

(2) J. C. Carter and R. W. Parry, *J. Amer. Chem. Soc.*, **87**, 2354 (1965).

Table I. Infrared Frequencies of $H_3BCO \cdot N(CH_3)_3$ from 3000 to 300 cm^{-1}

$H_3BCO \cdot N(CH_3)_3$	Tentative assignment	$H_3BCO \cdot N(CH_3)_3$	Tentative assignment
2955, w	ν(C–H)	1060, sh, w	
2400, s	ν(B–H)	993, s	w(CH$_3$)
2335, sh, m	ν(B–H)	975, m	ν(N–CH$_3$)
2295, s	ν(B–H)	890, s	r(BH$_3$)
2258, sh, w	ν(B–H)	880, sh, m	
1798, s	ν(C=O)	870, m	
1478, s	δ(CH$_3$)	824, s	ν(N–CH$_3$)
1463, m	δ(CH$_3$)	802, sh, m	
1397, w	δ(CH$_3$)	770, s	ν(C–N)
1255, w	r(CH$_3$)	534, s	t(BH$_3$)
1241, w	r(CH$_3$)	495, s	
1162, m	δ(BH$_3$)	480, sh, m	
1143, sh, w		418, s	ν(B–C)
1110, w	δ(BH$_3$)	358, m	
1094, m	t(CH$_3$)	323, m	

the $(CH_3)_3N \cdot OCBH_3$ to be sublimed under low pressures and made it possible to obtain the infrared spectrum at −180°. Boron-11 nmr spectra were obtained in solution at low temperatures.

The infrared and boron nmr spectra of trimethylamine–carbon monoxide–borane support the structure with the amine nitrogen bonded to the carbon atom of H_3BCO. Infrared data and tentative assignments are shown in Table I. The CO stretching vibration in the known boranocarbamates[2] occurs in the region 1630–1640 cm^{-1} and at 1635 cm^{-1} for the isoelectronic and comparable N-methylacetamide. Data which are analyzed in more detail elsewhere[3] permit the assignment of the 1790–1800-cm^{-1} band of $(CH_3)_3N \cdot H_3BCO$ to the ν_{CO} mode. This is where the band would be expected for the less stable base adduct because ν_{CO} for uncomplexed H_3BCO occurs at 2165 cm^{-1}. These data plus others support the usual generalization that removal of electron density from the carbon increases the frequency of the ν_{CO} band (less electron density in the antibonding CO orbitals) whereas increasing electron density on the carbon decreases the value of ν_{CO} (more antibonding electrons in CO). On this basis the band at 1790–1800 cm^{-1} is very close to that predicted for ν_{CO} in $(CH_3)_3N \cdot H_3BCO$ and offers strong support for the structure proposed.

The ^{11}B nmr spectrum of $H_3BCO \cdot N(CH_3)_3$ in ethyl ether solution shows the expected 1:3:3:1 quartet from spin–spin coupling of boron and the three equiv-

(3) J. C. Carter, G. W. Luther III, and A. L. Moyé, *Appl. Spectrosc.*, in press.

alent hydrogens (J_{BH} = 105 Hz, same for H_3BCO). Chemical shift values move slightly to lower fields in the series H_3BCO (neat), H_3BCO (ethyl ether), and $H_3BCO \cdot N(CH_3)_3$ (ethyl ether). This may be interpreted as indicating weak complex formation between H_3BCO and $(C_2H_5)_2O$ of the same nature as the adduct $H_3BCO \cdot N(CH_3)_3$. Because the chemical shift is intermediate between neat H_3BCO and $H_3BCO \cdot N(CH_3)_3$, it may be interpreted that $N(CH_3)_3$ acts as a stronger Lewis base to H_3BCO than $(C_2H_5)_2O$ as expected. This is in agreement with the experimental observation that no complex of composition $H_3BCO \cdot (C_2H_5)_2O$ could be isolated under the conditions used for preparation and isolation of $H_3BCO \cdot N(CH_3)_3$. Compared to neat H_3BCO and H_3BCO in ethyl ether, substantial quadrupolar broadening is noted for $H_3BCO \cdot N(CH_3)_3$.

All data support the structure

$$(CH_3)_3N \longrightarrow C \overset{\displaystyle O}{\underset{\displaystyle BH_3}{\big\langle}}$$
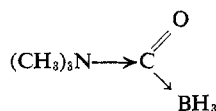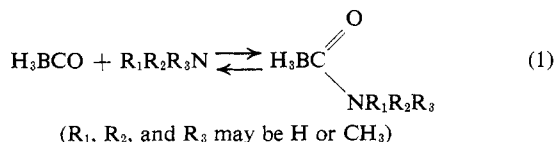
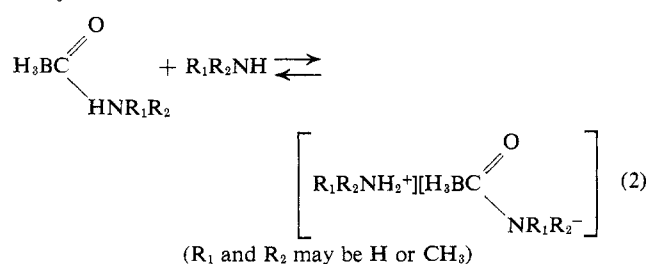which may be considered as an analog of the still unknown carbamic acid.

Chemical evidence also supports this structure. It is assumed that the BCO chain remains intact. The low temperature ($-126°$) at which the reaction occurs does not lend itself to drastic molecular rearrangements. This assumption is further supported by recovery of H_3BCO on careful warming of the adduct. We thus find the carbon atom to be unique in this three-coordinate position; it functions as a Lewis base to the borane fragment but must necessarily be acting as a Lewis acid to the trimethylamine molecule.

Attempts to prepare a 1:1 adduct involving carbon monoxide–borane and methylamine were unsuccessful. Only methylammonium N-methylboranocarbamate and the excess carbon monoxide–borane were isolated. Apparently rapid proton transfer occurs even at $-126°$.

The results of the trimethylamine study are in agreement with the following mechanism for the low temperature reaction of H_3BCO with ammonia and amines to form the boranocarbamate salts. The reaction could occur by first coordination of the amine or ammonia molecule to the carbon atom of the carbon monoxide–borane (eq 1). Proton transfer, if possible, from the coordinated amine to a second amine or ammonia molecule could then take place in a second step (eq 2).

$$H_3BCO + R_1R_2R_3N \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} H_3BC \overset{\displaystyle O}{\underset{\displaystyle NR_1R_2R_3}{\big\langle}} \qquad (1)$$

(R_1, R_2, and R_3 may be H or CH_3)

If R_3 is H

$$H_3BC \overset{\displaystyle O}{\underset{\displaystyle HNR_1R_2}{\big\langle}} + R_1R_2NH \rightleftharpoons$$

$$\left[R_1R_2NH_2^+ \right]\left[H_3BC \overset{\displaystyle O}{\underset{\displaystyle NR_1R_2^-}{\big\langle}} \right] \qquad (2)$$

(R_1 and R_2 may be H or CH_3)

At higher temperatures the reaction of H_3BCO and $(CH_3)_3N$ proceeds by base displacement to liberate carbon monoxide. This may be explained in two ways. The displacement reaction may be too slow to be observed at low temperatures or it may require prior dissociation of H_3BCO to diborane (or BH_3 groups) and CO with subsequent reaction with trimethylamine to yield trimethylamine–borane. Our observations do not serve to distinguish between these possibilities. Apparently the initial reaction temperature ($-78°$) selected by Burg and Schlesinger was sufficiently high that adduct formation was not observed and sufficiently low that base displacement did not take place to any measurable degree. Thus they observed no reaction between H_3BCO and $(CH_3)_3N$ under these conditions.

The triethylamine–carbon monoxide–borane adduct could not be sublimed without decomposition, and the triphenylphosphine adduct prepared in ether could not be isolated in a solvent free condiion. No evidence for reaction between carbon monoxide–borane and pyridine was observed at low temperatures.

Experimental Section

Reagents and Techniques. BH_3CO was prepared by literature methods.[1,2] It was stored at $-196°$ and measured and transferred as rapidly as possible to avoid decomposition.

Trimethylamine was obtained from Matheson Co. It was distilled from $-83.6°$ and the first volatile fraction discarded. It was then dried over P_4O_{10} for several days prior to use. Triethylamine (Eastman Chemical Company) was distilled and dried over P_4O_{10} prior to use. Pyridine (reagent grade) was distilled in a vacuum line prior to use. Ethyl ether was anhydrous reagent grade dried over calcium hydride. Methyl ether (Matheson Co.) was dried over calcium hydride. All reactions were conducted using standard vacuum line techniques and equipment.[4]

The ^{11}B nmr spectra were taken at 32.1 MHz using a Varian HA-100. Samples were sealed in 5-mm tubes, and the spectra were referenced to $(CH_3)_3B$ as an external standard. All spectra reported were taken at $-65°$.

Infrared Spectra. The infrared spectra were taken on a Beckman IR-10 at approximately $-180°$ in a low temperature cell with CsI optics. The spectra were measured between 4000 and 250 cm^{-1} using a polystyrene film for calibration. The values given for absorption bands are accurate to ± 8 cm^{-1} over the region 4000–2000 cm^{-1} and ± 4 cm^{-1} over the region 2000–250 cm^{-1}.

Reaction of H_3BCO and Trimethylamine in Methyl Ether. In a typical reaction 1.84 mmol of BH_3CO and 3.51 mmol of trimethylamine were condensed in a reaction tube with 3 ml of methyl ether. The reaction was allowed to proceed for 2 hr at $-111°$. At this time approximately 1% of the BH_3CO had decomposed to yield carbon monoxide. The solvent was removed at $-111°$ and the remaining material carefully fractionated to yield a compound of the composition $H_3BC(O)N(CH_3)_3$. The fractionation proved difficult and yields were relatively poor compared to the direct reaction described below.

Direct Reaction of H_3BCO and Trimethylamine. In a typical reaction identical amounts of carbon monoxide–borane and trimethylamine, approximately 0.4 mmol of each, were allowed to react at $-126°$ for 2.5 hr. Only a trace of noncondensable gas had formed at this time. Material volatile at $-126°$ was removed; then material volatile at $-111°$ and finally $-95°$ was removed. The product, $H_3BC(O)N(CH_3)_3$, was obtained in nearly quantitative yield by sublimation from the reaction tube at $-63°$. Only a trace of trimethylamine–borane remained in the tube. The compound was analyzed by condensing a sample in a weighed bulb and allowing it to decompose at room temperature to yield carbon monoxide and trimethylamine–borane. In a typical experiment 3.95 mg of compound gave 0.0406 mmol of carbon monoxide. This represents 97.3 g of sample per mole of carbon monoxide in comparison to 101.0 g of $BH_3C(O)N(CH_3)_3$ expected to yield 1 mol of carbon monoxide. In a second sample 40.5 mg of $H_3BC(O)-N(CH_3)_3$ produced 0.3858 mmol of carbon monoxide on decom-

(4) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

position. This is equivalent to 105 g of sample per mole of carbon monoxide liberated. The solid obtained from decomposition was shown by its molecular weight and its low temperature infrared spectrum to be trimethylamine–borane. Carbon monoxide was identified by its molecular weight and its infrared spectrum. No other products were observed. The infrared spectrum of the solid obtained by direct reaction was identical with that obtained when the reaction was allowed to take place in methyl ether. The composition of the adduct was also demonstrated by using excess trimethylamine in the reaction and analyzing the recovered excess by formation of trimethylammonium halides.

Evidence for Dissociation of $H_3BC(O)N(CH_3)_3$. A sample of $H_3BC(O)N(CH_3)_3$ was warmed very rapidly to room temperature, its pressure measured quickly, and the sample immediately cooled to $-196°$. The carbon monoxide which had formed was removed and the remainder of the sample was transferred to a weighing bulb. The apparent molecular weight of the gas was 51.1. If the sample had not been dissociated, the molecular weight expected for H_3-

BCO·$N(CH_3)_3$ would be 101.0. If it had dissociated into two particles, the apparent molecular weight would then be 50.5. It is concluded that the dissociation products are H_3BCO and trimethylamine. If dissociation had occurred to yield trimethylamine–borane and carbon monoxide directly, the very low vapor pressure of the trimethylamine–borane at room temperature would have resulted in only half the total pressure observed. When a sample was warmed very rapidly and allowed to stand, the pressure reached a maximum and then dropped to approximately half of the value as a reaction took place with the visible formation of trimethylamine–borane in the reaction tube.

A Study of the Reactions of Diborane with Several Polydimethylaminoalanes and Related Compounds. The Synthesis and Chemistry of $H_2B(NMe_2)_2Al(BH_4)_2$

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Abstract: Excess B_2H_6 reacts with Et_2O solutions of $Al(NMe_2)_3$, $HAl(NMe_2)_2$, or $[H_2B(NMe_2)_2]_2AlH$ to form the new compounds $H_2B(NMe_2)_2Al(BH_4)_2$ and μ-$[Me_2N]_2B_3H_7$ in addition to $Me_2NAl(BH_4)_2$, $Et_2OAl(BH_4)_3$, $(Me_2$-$NBH_2)_2$, and μ-$Me_2NB_2H_5$. The compound $H_2B(NMe_2)_2Al(BH_4)_2$ reacts slowly with B_2H_6 in Et_2O to form μ-Me_2-NB_2H_5 and $Et_2O·Al(BH_4)_3$. Reaction with 1 mol of $P(C_6H_5)_3$ affords $H_2B(NMe_2)_2AlH(BH_4)$ and $(C_6H_5)_3PBH_3$, while excess Me_3N gives $[H_2B(NMe_2)_2]_2AlH$, Me_3NBH_3, and an inseparable mixture of Me_3N complexes of aluminum hydridoborohydrides. A study of the stepwise addition of B_2H_6 to $Al(NMe_2)_3$ shows that treatment with 0.5 mol of B_2H_6 yields approximately equal quantities of $HAl(NMe_2)_2$ and $[H_2B(NMe_2)_2]_2AlH$. Reaction of HAl-$(NMe_2)_2$ with 1 mol of B_2H_6 produces $H_2B(NMe_2)_2AlH(BH_4)$, while reaction of $[H_2B(NMe_2)_2]_2AlH$ with 1 mol of B_2H_6 gives $H_2B(NMe_2)_2AlH(BH_4)$ and $(Me_2NBH_2)_2$. Diborane and $H_2B(NMe_2)_2AlH(BH_4)$ form $H_2B(NMe_2)_2Al$-$(BH_4)_2$, μ-$Me_2NB_2H_5$, $Me_2NAl(BH_4)_2$, and a small quantity of μ-$(Me_2N)_2B_3H_7$.

Relatively little is known of the chemistry of mixed boron–aluminum compounds, and their systematic preparation is a challenging synthetic problem. The recent studies by Schram and his colleagues[1] and the earlier work by Ruff[2,3] on aminoboron–aluminum hydrides have amply demonstrated the chemical and structural complexity of this field. In this laboratory the study of boron–aluminum chemistry commenced with the investigation of the action of B_2H_6 on amine- and aminoalanes,[4] which took form as a supplement to an investigation of the reactions of B_2H_6 with tris-(amino)boranes[5] and as part of a general interest in the synthesis and study of heteroatom substituted boranes. An account of the early phase of this work appeared in 1972 which detailed the reactions of B_2H_6 with Me_3NAlH_3 and $(Me_2NAlH_2)_3$.[4] In these relatively

simple systems the rapid formation of aluminum borohydride derivatives by addition of diborane to the Al–H bond was followed by slow aluminum–nitrogen bond cleavage to afford $Et_2OAl(BH_4)_3$ and Me_3NBH_3 and μ-$Me_2NB_2H_5$, respectively, on prolonged exposure to excess B_2H_6. It was anticipated that the reactions of $HAl(NMe_2)_2$ and $Al(NMe_2)_3$[6] with B_2H_6 would be more complex and would provide an illuminating comparison with the analogous reactions of $HB(NMe_2)_2$ and $B(NMe_2)_3$ with B_2H_6.[7] The action of excess B_2H_6 on $Al(NMe_2)_3$ in Et_2O produces, among other products, the new B–N–Al heterocycle $H_2B(NMe_2)_2Al(BH_4)_2$,[8] the chemistry of which is partly the subject of this paper. The discovery that $HAl(NMe_2)_2$ and $[H_2B(NMe_2)_2]_2$-

(1) R. E. Hall and E. P. Schram, *Inorg. Chem.*, **10**, 192 (1971), and earlier papers.
(2) J. K. Ruff, *Inorg. Chem.*, **2**, 515 (1963).
(3) J. K. Ruff, *Inorg. Chem.*, **1**, 612 (1962).
(4) P. C. Keller, *Inorg. Chem.*, **11**, 256 (1972).
(5) L. D. Schwartz and P. C. Keller, *J. Amer. Chem. Soc.*, **94**, 3015 (1972).

(6) In Et_2O tris(dimethylamino)alane is reported to be monomeric, while bis(dimethylamino)alane was suggested to be in monomer–dimer equilibrium: E. Wiberg and A. May, *Z. Naturforsch.*, **10b**, 234 (1955). Similarly, dimethylaminoaluminum borohydride is known to be associated in benzene (ref 2) but its state of aggregation in Et_2O is uncertain. In this paper these compounds will be written as monomers.
(7) P. C. Keller, *J. Amer. Chem. Soc.*, **96**, 3078 (1974)
(8) P. C. Keller, *J. Amer. Chem. Soc.*, **94**, 4020 (1972).