Contribution from the Richard B. Wetherill Laboratory,
Purdue University, West Lafayette, Indiana 47907

Molecular Addition Compounds. 4. Unusually Slow Reaction of Tertiary Amines with 9-Borabicyclo[3.3.1]nonane (9-BBN) Dimer. New, Stable, Mildly Reactive Amine Complexes of 9-BBN[1]

HERBERT C. BROWN* and SURENDRA U. KULKARNI[2]

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The complexation of 9-borabicyclo[3.3.1]nonane (9-BBN) dimer with representative tertiary amines, such as trimethylamine (Me_3N), pyridine (py) and γ-picoline (γ-Pic), proceeds to completion, providing as products stable 9-BBN·amine complexes. In contrast, other bases which are more sterically demanding or weaker, such as triethylamine (Et_3N), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), and methyl sulfide (Me_2S), fail to form such stable adducts. In these cases, a mobile equilibrium exists involving the base and the complexed and the uncomplexed 9-BBN species. Unexpectedly, the rate of reaction of these amines with 9-BBN dimer is relatively slow, corresponding to a rate-determining step involving the dissociation of the dimer into monomer. The stable 1:1 amine complexes of 9-BBN have been isolated and characterized. In contrast to related H_3B·amine complexes, these 9-BBN addition complexes are quite reactive toward ethanol and other protonic sources. 9-BBN·py reveals interesting properties as a reducing agent but is relatively inert as a hydroborating agent under similar experimental conditions. The ^{11}B chemical shifts of 9-BBN addition compounds can be related to the strengths and reactivities of these complexes.

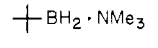
Introduction

The first borane–amine complex to be reported was borane–trimethylamine (**1**) prepared by the fast direct reaction of diborane with trimethylamine (Me_3N) (eq 1).[3] Since then,

$$\underset{}{B_2H_6 + 2Me_3N \rightarrow 2\underset{\mathbf{1}}{H_3B\cdot NMe_3}} \qquad (1)$$

numerous amine complexes of borane have been prepared, and their application to organic synthesis has been examined.[4] Such borane–amines are generally highly stable compounds applicable in reduction and hydroboration reactions.[4] Except for the less stable, more reactive borane–*N*-arylamine complexes, all other borane–amines hitherto known are stable in hydrolytic solvents at neutral pH.[5]

In recent years a number of partially substituted boranes have been prepared and have proved to be highly useful reagents.[6] With few exceptions, such as *tert*-butylborane–trimethylamine (**2**),[7,8] phenylborane–pyridine (**3**),[9] thexylborane–trimethylamine (**4**),[10] and disiamylborane–trimethylamine (**5**),[10] the preparation and the chemistry of the corresponding amine complexes have remained relatively unexplored until recently. However, recent studies in this laboratory have resulted in simple procedures for the preparation of thexylborane–triethylamine (**6**),[11] cyclohexylborane–triethylamine (**7**),[11,12] DIBborane·TMEDA (**8**),[13] and isopinocampheylborane–triethylamine (**9**)[14] and have led to the discovery of promising new applications for these derivatives.



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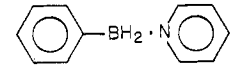

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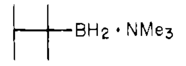

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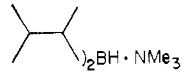

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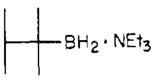

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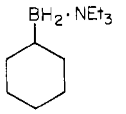

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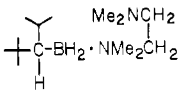

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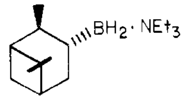

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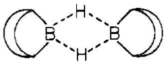
An exceptionally interesting hydroborating and reducing agent among the partially substituted boranes is 9-borabicyclo[3.3.1]nonane (9-BBN) (**10**).[6,15,16] Its favorable physical properties combined with its unusual stability have made 9-BBN the only commercially available dialkylborane.[17] In view of its high regioselectivity in the hydroboration of olefins[15] and its selective reducing properties,[16] it appeared possible that suitable amine complexes of 9-BBN would modify its characteristics and provide better and milder reagents for these purposes. Accordingly, we undertook to study the stoichiometry of the reaction of **10** with various amines and to prepare and examine such derivatives. In the course of this study, we observed that the complexation stage was unusually slow. Consequently, we measured the rates of reaction of representative tertiary amines with **10**. Three stable amine complexes, 9-BBN·NMe_3 (**11**), 9-BBN·py (**12**), and 9-BBN·γ-Pic (**13**), have been prepared and characterized. However, in the case of more sterically demanding or weaker bases, such as Et_3N, TMEDA, and Me_2S, the reactions do not go to completion but proceed to a mobile equilibrium involving the reactants, as revealed by spectroscopic studies.



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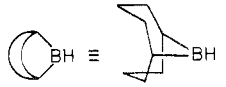


10A

Experimental Section

Materials. Pyridine, γ-picoline, and triethylamine were distilled from barium oxide and TMEDA was distilled from calcium hydride. Trimethylamine obtained from Eastman Organic Chemicals Co. and crystalline 9-BBN dimer obtained from Aldrich Chemical Co. were used directly. When the solution of 9-BBN in pentane was prepared, some insoluble material remained. This solution was filtered through an in-line filter.[18] The solvents, THF, pentane, ether, etc., were purified as described elsewhere.[18]

Methods. The reaction flask and other glassware employed for the experiments were dried in an oven and assembled in a stream of nitrogen. The special experimental techniques used in handling air-sensitive materials are described in detail elsewhere.[18] All melting points are uncorrected and were determined in evacuated, sealed capillary tubes using the Thomas-Hoover capillary melting point apparatus.

In a typical reaction set-up for the determination of rate and stoichiometry of complexation, a 25-mL round-bottom flask with a side arm for septum inlet, equipped with a magnetic stirring bar and a connecting tube, was charged with 5 mmol of 9-BBN solution in the respective solvent (THF, CCl_4, or $CDCl_3$). While stirring the contents at 25 °C, the calculated quantity of amine was added. At appropriate intervals of time, aliquots were withdrawn for IR or NMR analysis.

Spectroscopic Methods. The ^1H and ^{11}B NMR spectra were recorded on the Varian T-60 and the XL-100 instruments, respectively.

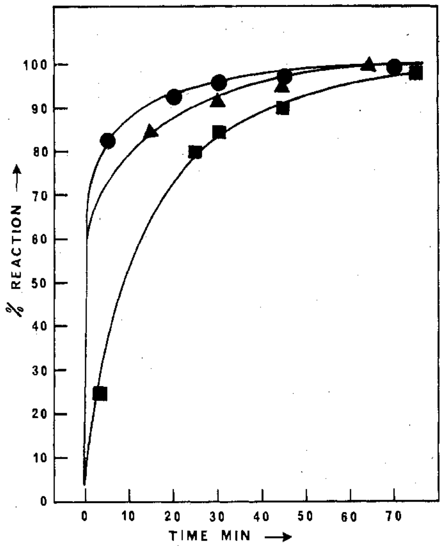


Figure 1. Rates of complexation, in THF at 25 °C, of 9-BBN dimer (0.275 M) with representative strong bases: ▲, γ-picoline (0.55 M); ●, pyridine (0.55 M); ■, NMe_3 (0.55 M).

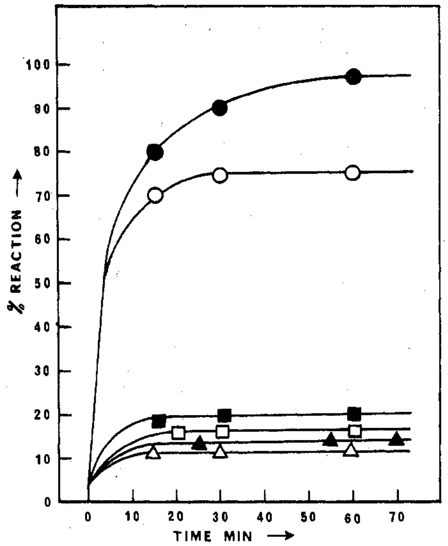


Figure 2. Rate and stoichiometry of the reaction, in THF at 25 °C, of 9-BBN (0.275 M in dimer) with weak or sterically more demanding bases: ○, TMEDA (0.275 M); ●, TMEDA (0.55 M); □, NEt_3 (0.55 M); ■, NEt_3 (1.1 M); △, SMe_2 (0.55 M); ▲, SMe_2 (1.1 M).

The ^{1}H and ^{11}B chemical shifts are in δ ppm with reference to Me_4Si and $F_3B{\cdot}OEt_2$ standards, respectively. The IR spectra were recorded on the Perkin-Elmer-700 infrared spectrophotometer using a sodium chloride cell. The same cell was used throughout this work. Standard solutions of various concentrations of 9-BBN (0.20, 0.30, 0.40, 0.50, and 0.58 M in monomeric species) in THF were prepared and the IR spectra recorded. A calibration curve was plotted with log T_0/T vs. concentration of 9-BBN (T_0 = percent transmittance of THF reference band at 1970 cm^{-1} and T = percent transmittance of the B–H–B bridge band at 1560 cm^{-1}). This calibration curve was used to calculate the concentration of unreacted 9-BBN from the value of log T_0/T for a particular aliquot.

Stoichiometry and Rate Studies. (a) Determination of Rate and Stoichiometry by IR. The reactions were carried out in THF, as described in the general procedure. The reaction of pyridine is representative. To 8.6 mL (5 mmol, 0.58 M) of a solution of 9-BBN in THF was added 0.415 mL (5 mmol) of pyridine with vigorous stirring. Aliquots were withdrawn at definite intervals of time and the IR spectra recorded. The values of log T_0/T were obtained from the spectra and the concentrations of unreacted 9-BBN in the aliquots were determined from the calibration curve. In this way the rates and extent of completion of the reactions of 9-BBN with pyridine, γ-picoline, Me_3N, Et_3N, TMEDA, and Me_2S could be followed (Figures 1, 2). By varying the ratio of amine to 9-BBN, the stoichiometry of the reaction could be examined (Figure 2).

(b) Determination of Rate and Stoichiometry by NMR. (1) Rate of Complexation with Me_3N. In the usual reaction flask 9.0 mL of 9-BBN solution in CCl_4 (0.55 M in monomer, 5.0 mmol) and 1.1 mL of a freshly prepared solution of Me_3N in CCl_4 (4.6 M solution, 5.0 mmol) were mixed. An aliquot was taken in a NMR tube, and the spectra were recorded at definite intervals of time. The sample once placed in the NMR tube was kept in the probe to maintain a constant temperature of 35 °C. From the integration of the Me_3N peak at δ 2.1 (uncomplexed) and 2.6 (complexed) the reaction rate can be followed and the stoichiometry of the reaction determined. On completion of the reaction, 0.1 mL (0.5 mmol, 10% excess) of Me_3N in CCl_4 was added. The NMR spectrum indicated that the excess Me_3N remained unreacted even after 15 h.

(2) Rate of Complexation with γ-Picoline. The procedure is similar to that described above, except that the reaction mixture was formed from 5.0 mmol of 9-BBN contained in 9.5 mL of $CDCl_3$ and 0.49 mL (5.0 mmol) of γ-picoline. From the integration of doublets at δ 7.0 (β protons in the uncomplexed γ-picoline) and 7.4 (β protons in the complexed γ-picoline), the rate of reaction can be followed. Any excess γ-picoline added remains unreacted as indicated by the δ 7.0 peak.

Preparation of Complexes. (a) 9-BBN·py (12). In a 1-L reaction flask[18] with side arm, connecting tube, and magnetic stirring bar, 25.0 g (205 mmol) of 9-BBN (crystalline)[17] was dissolved in about 400 mL of pentane and filtered through an in-line filter (under nitrogen, using double-ended needle).[18] To the well-stirred solution was added dropwise 17.8 mL (220 mmol) of pyridine and the stirring continued for 1.5 h at room temperature. On cooling to 0 °C, crystals separate. Sometimes the crystals start depositing even while stirring at room temperature. Supernatant liquid was decanted and the product washed with pentane and dried under the aspirator vacuum: 34.5 g, mp 74–75 °C, a yield of 86%. Recrystallization from a mixture of Et_2O and pentane provided 29.2 g (a yield of 86% in crystallization) of colorless, shining crystals, mp 75.5–76.0 °C. Integration in ^{1}H NMR indicated that it is a 1:1 complex. ^{11}B NMR spectrum shows an unresolved peak (no doublet) at δ +1.0. IR shows absence of the B–H–B bridge band at 1560 cm^{-1} but the presence of an unbridged B–H band at 2300 cm^{-1}. The product gives excellent C, H, N analyses, mol wt (benzene) 204.

(b) 9-BBN·γ-Pic (13). In a 250-mL reaction flask with the usual setup, 71.4 mL (0.42 M, 30 mmol) of a 9-BBN solution in pentane was placed. While stirring, 3.2 mL (33 mmol) of γ-picoline was added and the stirring continued for 1.5 h at room temperature with the formation of a white precipitate. The reaction mixture was cooled in an ice bath and the supernatant liquid was removed through a double-ended needle. The product was recrystallized from a mixture of $CHCl_3$ and pentane and dried under the aspirator vacuum. There was obtained 4.4 g of the complex, a yield of 69%, mp 116–117 °C, ^{1}H NMR integration agreed perfectly with the structure; ^{11}B NMR spectrum shows an unresolved hump (no doublet) at δ +1.2; the IR spectrum reveals no B–H–B bridge band at 1560 cm^{-1} but only the B–H band at 2300 cm^{-1}.

(c) 9-BBN·NMe_3 (11). Using the same experimental setup as described in (b), 119 mL of the 9-BBN solution in pentane (0.43 M, 50 mmol) and 14 mL of Me_3N in pentane (4.0 M, 56 mmol) were mixed. Following stirring for 1.5 h at room temperature, about half of the solvent was pumped off. Cooling in an ice–salt mixture afforded colorless crystals. The product was recrystallized from pentane and dried by passing a stream of nitrogen over the crystals. There was obtained 4.4 g, mp 74–75 °C, an overall yield of 49%. ^{1}H NMR spectrum indicates that the product is a 98% pure complex; IR spectrum exhibits only the 2200–2300-cm^{-1} band, with no absorption at 1560 cm^{-1}; ^{11}B NMR δ −3.9 (doublet, J_{BH} = 80 Hz).

Solubility of Complexes. As a representative case, the solubility of 9-BBN·py (12) was determined in common organic solvents. In a typical experiment, a 25-mL reaction flask was equipped as described in the general procedure, and about 5 g of the complex was transferred to the flask in a glovebag. Using a syringe, a minimum quantity of respective solvent was added and stirred for 0.5 h to ensure the complete equilibration. Each time 1.0 mL of the clear aliquot (5.0 mL in the case of pentane and CCl_4) was protonolyzed with a 1:1 mixture of MeOH and THF, and the volume of hydrogen liberated was measured in a gas buret.[18] The complex (12) was found to be readily soluble in more polar solvents: THF > 3.0 M, $CHCl_3$ ~3.0

M, Et_2O 1.8 M, pentane 0.15 M, and CCl_4 0.05 M at ambient room temperatures.

Protonolysis of Complexes. For the protonolysis of a solid complex, the purified complex was weighed into a 50-mL round-bottom flask connected to a gas buret.[18] While stirring vigorously, 25 mL of absolute ethanol was added and the volume of the hydrogen evolved was measured. The weight of the complex and the volume of hydrogen evolved are as follows: 1.24 g (6.85 mmol) of **11**, 176 mL (6.84 mmol); 1.53 g (7.61 mmol) of **12**, 194 mL (7.64 mmol); 1.73 g (8.05 mmol) of **13**, 203 mL (8.12 mmol).

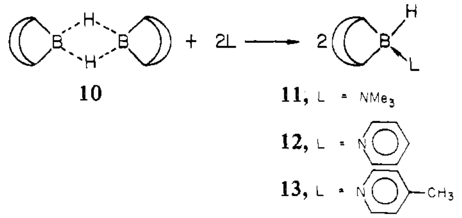
For the protonolysis of complex **12** with various protic substances in THF solutions (0.25 M in each reactant), similar experimental setup as described above was employed. The protonolysis with acetic acid is described as representative. A 50-mL round-bottom flask with a side arm and magnetic stirring bar was connected to a gas buret under nitrogen, and 2.22 mL (1.35 M solution, 3 mmol) of **12** in THF and 9.6 mL of THF were placed in the flask. While stirring, 0.172 mL (3 mmol) of glacial acetic acid was added and the volume of hydrogen evolved was measured at definite time intervals. Similarly, the rates of protonolysis of **12** with benzoic acid, ethanol, and water at 25 °C in 0.25 M solutions in THF were also determined.

Hydroboration with 9-BBN·py. The hydroboration of cyclopentene is representative. A 100-mL reaction flask with the usual setup was charged with 4.7 mL (2.13 M solution, 10 mmol) of **12** and 34.4 mL of THF. While stirring vigorously, 0.885 mL (10 mmol) of cyclopentene was added. At definite intervals of time, 5.0-mL aliquots were removed from the reaction mixture and hydrolyzed with a 1:1 mixture of methanol and THF. From this value, the residual hydride can be calculated and thus the rate of hydride uptake determined.

Reduction with 9-BBN·py. The rates of reduction of benzaldehyde, benzoyl chloride, and benzoic acid with **12** were followed in the same way as described for the determination of the rates of hydroboration. For benzoic acid and benzoyl chloride, the rates were also determined when reacted with 2 equiv of **12**.

Results and Discussion

Stoichiometry. In the case of relatively strong, unhindered amines, such as pyridine, γ-picoline, and trimethylamine, the reaction proceeded simply to the formation of the 1:1 complex (eq 2) (Figure 1). Any excess amine over the 1:1 stoichiometry remained unreacted. The course of the reaction could be followed by the IR and ^1H NMR spectroscopic methods (in these cases excess amine does not undergo rapid exchange on the NMR time scale). However, the more sterically demanding amines like Et_3N and TMEDA, or the weaker bases, such as Me_2S, fail to form such stable adducts (Figure 2). In these cases, a mobile equilibrium exists involving the base and the complexed and the uncomplexed 9-BBN species. The equilibrium can be completely shifted toward the formation of the complex 9-BBN·TMEDA (**14**) by adding 2 mol of TMEDA to 1 mol of 9-BBN dimer (**10**), so that the ratio of B:N is 1:2. However, the equilibrium is far less sensitive to the amount of base in the cases of Et_3N and Me_2S (Figure 2).



(2)

10

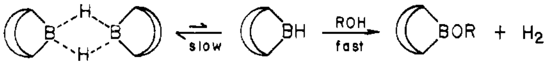
11, L = NMe_3

12, L =

13, L =

Reaction Rates. An unexpected feature in the reaction of tertiary amines with 9-BBN dimer was the apparently slow reaction observed, particularly in the formation of the complex with the three strong amines (eq 2). In all of the previous cases, the reaction of amines with diborane and its derivatives appeared to be fast, essentially instantaneous. There is no specific mention in the literature regarding measurable rates of complexation of boranes with amines. Indeed, it was observed that B_2H_6 is rapidly absorbed by Me_3N at very low temperature[3] to form **1**. More recently, the gas-phase reaction rates for the coordination of BH_3 with Me_3N,[19] BF_3 with NH_3,[20] and BF_3 with Me_3P[21] were found to be of the order of 10^{10} L mol^{-1} s^{-1}. Therefore, an attempt was made to determine the rates of the reaction of tertiary amines with **10**.

It is interesting to note that about 80–90% of the complex is formed in 10–15 min. This is comparable to the rates of alcoholysis[16a] of **10** with methanol, 1-hexanol, 3-ethyl-3-pentanol, phenol, 2,6-dimethylphenol, etc., and of **10** with reactive olefins.[16b] Such a striking similarity in the rate of reaction with alcohols, phenols, and olefins of widely different structural types is attributed to the fact that the rate-determining step must be the slow dissociation of the dimer into the monomer (eq 3).[16] The same explanation can be given



(3)

for the reaction of the tertiary amines with 9-BBN dimer at essentially the same rate.

Determination of Rate and Stoichiometry by NMR. The rates of reaction of **10** with Me_3N or with γ-picoline could be easily followed by ^1H NMR in CCl_4 and $CDCl_3$, respectively. The methyl protons in **11** (δ 2.6) and those in free Me_3N (δ 2.1) are well separated. As there is no fast (on the NMR time scale) exchange of Me_3N between **11** and the free amine, two individual peaks can be distinctly observed. By integrating these peaks, the amount of complexed and uncomplexed Me_3N can be calculated.

Similarly, integrating the doublets of the β protons in the complexed (δ 7.4) and the uncomplexed (δ 7.0) γ-picoline makes possible the calculation of the reaction rate. It should be noted that coordination of γ-picoline with 9-BBN shifts the β protons downfield without affecting the position of the α protons, probably attributable to the anisotropy of the $N \rightarrow B$ coordinate bond.[9]

Determination of Rate and Stoichiometry by IR. It is well established that the IR spectrum of 9-BBN dimer (**10**) has a strong absorption band at 1560 cm^{-1} arising from the B–H–B bridge structure.[15,22] This band disappears in the reaction with amines (eq 2) to form the monomer–amine complexes. Therefore, the rate of disappearance of the 1560-cm^{-1} band is identical with the rate of complexation. The 1970-cm^{-1} band of THF is utilized as a reference.

The rates of reactions of 9-BBN dimer with the various bases, pyridine, γ-picoline, Me_3N, Et_3N, TMEDA, and Me_2S, in the stoichiometric ratio followed in this way are shown in Figures 1 and 2.

Preparation of Complexes. The stable 1:1 molecular addition compounds **11**–**13** are isolated and characterized by physical methods such as IR, ^1H NMR, and ^{11}B NMR spectroscopy and also by some chemical methods like protonolysis.

To achieve a convenient preparation and isolation of the 1:1 addition compounds requires a careful selection of appropriate solvents. In THF the reaction of pyridine proceeds well, but the product is highly soluble, >3 M. This causes difficulties in its isolation. This problem was overcome by utilizing a nonpolar solvent, pentane, which possesses the desired characteristics. 9-BBN dimer is fairly soluble in pentane (0.45–0.50 M in monomer), while the more polar complex **12** is considerably less soluble (0.15 M). Addition of 2 mol of pyridine to 1 mol of **10** (dimer) in pentane at 25 °C, with adequate time to permit completion of the reaction (~1.5 h), provides **12**. This crystallizes out on cooling to 0 °C.

In the case of γ-picoline, complex **13** precipitates on stirring for some time, even without cooling, but **11** fails to separate, even on cooling, from the reaction mixture. However, **11**, which is relatively more soluble in pentane, can be isolated by pumping off about half of the solvent, followed by cooling

Table I. Reaction of 9-BBN·py with Representative Compounds at 25 °C[a]

Compd	Time, min	Amt of hydrogen evolved[b]	Amt of hydride used for reduction[b]
Water	5	0.59	0.00
	10	0.76	0.00
	15	0.86	0.00
	30	0.97	0.00
Acetic acid	5	0.82	0.00
	10	0.88	0.00
	15	0.94	0.00
Benzoic acid	5	0.71	0.00
	10	0.85	0.00
	15	0.94	0.00
Benzoic acid[c,d]	10	1.00	0.00
	30	1.00	0.00
	60	1.00	0.00
	180[e]	1.00	0.00
Ethanol	5	0.58	0.00
	10	0.72	0.00
	15	0.82	0.00
	20	0.96	0.00
1-Hexene	60	0.00	0.03
	240	0.00	0.28
	600	0.00	0.41
Cyclopentene	30	0.00	0.02
	60	0.00	0.06
	300	0.00	0.09
Benzoyl chloride[d]	10	0.00	1.00
Benzoyl chloride[c]	5	0.00	1.84
	10	0.00	1.92
	15	0.00	1.98
Benzaldehyde	2	0.00	0.16
	10	0.00	0.56
	20	0.00	0.81
	45	0.00	0.88
	60	0.00	1.00

[a] The reaction mixture is 0.25 M in the compound and 0.25 M in 9-BBN·py, in THF solution. [b] Units are mmol/mmol of compound. [c] The reaction mixture is 0.25 M in the compound and 0.50 M in 9-BBN·py. [d] Reaction in $CDCl_3$, rate followed by ^1H NMR. [e] Reaction at 50 °C.

to −15 °C. The product must then be dried by passing nitrogen over the crystals, rather than by applying vacuum, which can cause a partial loss of the amine. Thus, **11** is a relatively weaker complex compared to **12** and **13**. It has been observed in the past that the Me_3N complex with disiamylborane is unstable and readily loses amine.[10]

^{11}B NMR Characteristics. The ^{11}B NMR spectrum of **10** has an unresolved signal at δ −27. This is shifted upfield on the formation of a complex. The complexes **11, 12,** and **13** have resonances at δ −3.9 (doublet, J_{BH} = 80 Hz), +1.0 (unresolved hump), and +1.2 (unresolved hump), respectively. Due to the relatively slow (on the NMR time scale) exchange of ligands between the complex and the free ligand, it is possible to observe ^{11}B chemical shifts for weaker complexes in the equilibrium mixtures, even though such complexes cannot be isolated in free form. Thus the ^{11}B chemical shifts for the complexes such as 9-BBN·TMEDA (**14**), 9-BBN·NEt_3 (**15**), and 9-BBN·SMe_2 (**16**) are δ −3.9 (doublet, partly resolved, J_{BH} = 87 Hz), −7.8 (unresolved hump), and −3.8 (doublet, J_{BH} = 107 Hz), respectively. The maximum amounts of complexed species (**15** and **16**) that can be attained by adding excess of corresponding bases are 20 and 50%, respectively, as observed from the approximate areas of ^{11}B NMR signals for these complexes. However, 2 mol of TMEDA reacts with 1 mol of **10** to form the complex **14** cleanly, although the attempts to isolate **14** have been futile.

The ^{11}B chemical shifts have been, in the past, correlated to the donor strengths of substituted pyridines in BH_3·py complexes (δ +12 to +20).[9] The chemical properties of these complexes compared to those of **11–13** (^{11}B chemical shifts δ −3 to +2) clearly indicate that the latter are weaker complexes and hence are more reactive than the former. Accordingly, still weaker complexes, **14–16**, have chemical shifts in the range of δ −3 to −8. Such a correlation between ^{11}B chemical shift and the strength of the complex is apparent, at least qualitatively.

Chemical Properties. Stability. The trimethylamine complex (**11**) is unstable in air, while **12** and **13** show no change in melting point after 3–4 h of exposure to atmosphere. The amine can partly be removed from **11** under the water aspirator vacuum (~15–20 mmHg), whereas **12** and **13** are quite stable under these conditions.

Protonolysis. An unexpected feature of the chemistry of these complexes is their ready protonolysis by ethanol or other protonic sources. In the past, addition compounds of borane have uniformly proven to be stable to water and ethanol. Thus some reductions with borane–amine complexes have been carried out in methanol or acetic acid media.[4] A further evidence for the stability of H_3B·py (**17**) to protic solvents is the application of **17** as a reducing agent in a mixture of methanol and acetic acid under reflux.[23] In contrast to these, the amine complexes of 9-BBN (**11–13**) are quite reactive toward water and ethanol. The representative complex **12** is only slightly less reactive than the parent 9-BBN toward protonolysis under similar conditions. The rates of protonolysis of **12** with water, ethanol, acetic acid, and benzoic acid are given in Table I.

Hydroboration. 9-BBN·py (**12**) is relatively inert as a hydroborating agent at 25 °C as revealed by the reaction with 1-hexene and cyclopentene (Table I).

Selective Reduction. As a selective reducing agent, **12** reveals interesting properties. Benzaldehyde is reduced to benzyl alcohol in approximately 1 h. Benzoyl chloride rapidly consumes 2 equiv of **12** and is reduced to the alcohol stage. However, benzoic acid evolves hydrogen, with no further reaction in several hours, even at 50 °C. Some possible applications of **11–13** as selective reducing agents are currently being explored.

Conclusions

This study describes the preparation of some reasonably stable but unexpectedly reactive 9-BBN·amine complexes. These possess promise as selective reducing agents in organic synthesis. An unusually slow rate of reaction between a borane and tertiary amine is observed for the first time. Evidently the amine cannot rupture the strong boron–hydrogen bridge in the 9-BBN dimer by direct attack but reacts only with monomer produced in a slow rate-determining dissociation of the dimer. The observed ^{11}B chemical shifts correlate with the chemical properties.

Registry No. 10, 280-64-8; **11**, 64070-34-4; **12**, 64045-95-0; **13**, 64045-94-9; **14**, 64045-93-8; **15**, 64045-92-7; **16**, 64045-91-6; water, 7732-18-5; acetic acid, 64-19-7; benzoic acid, 65-85-0; ethanol, 64-17-5.

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Contribution from the Department of Chemistry, University of Virginia,
Charlottesville, Virginia 22901

New Chemistry of the Iron Dihydrogen Metallocarborane $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$. Reaction with CO and Cage Insertion of Germanium, Tin, and Cobalt

WILLIAM M. MAXWELL, KWAI-SAM WONG, and RUSSELL N. GRIMES*

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The reaction of the title compound with carbon monoxide gas at 200 °C and 1.6 atm produced in good yield a ten-vertex dicarbon ferracarborane, $2,1,4\text{-}(CO)_3Fe(CH_3)_2C_2B_7H_7$, an analogue of *closo*-$C_2B_8H_{10}$. The $[(CH_3)_2C_2B_4H_4]_2FeH^-$ anion reacted with GeI_2 and with $SnCl_2$ to give $M^{IV}Fe(CH_3)_4C_4B_8H_8$ (M^{IV} = Ge or Sn), each product containing a "bare" germanium or tin atom; treatment of the same anion with $PbBr_2$ gave the tetracarbon carborane $(CH_3)_4C_4B_8H_8$. From ^{11}B and ^1H data and electron-counting arguments, the structures of these electron-hyperdeficient $M^{IV}Fe(CH_3)_4C_4B_8H_8$ systems are proposed to consist of two seven-vertex pentagonal bipyramids fused at a common iron vertex with an additional atom wedged between the polyhedra, as in the analogous $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$ structure reported earlier by Maxwell, Sinn, and Grimes. However, in the germanium and tin complexes the metal atom is proposed to occupy the wedging position, in contrast to the established Fe–Co structure in which the metal is in the equator of one of the polyhedra. Treatment of the title compound with $CoCl_2$ and cyclopentadiene in ethanolic KOH produced a mixture of cobaltaferracarboranes, cobaltacarboranes, iron(III) ferracarboranes, and a *B*-diethoxy derivative of the tetracarbon system $(CH_3)_4C_4B_8H_8$. The major new products were $\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)Fe^{III}(CH_3)_2C_2B_4H_3$, $(\eta^5\text{-}C_5H_5)Fe^{III}(CH_3)_2C_2B_4H_4$, $\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)\text{-}Co(CH_3)_4C_4B_7H_6$, and $(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]FeH_2[(CH_3)_2C_2B_4H_4]$, with smaller amounts of $1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)\text{-}Co[(CH_3)_2C_2B_3H_3]FeH(\eta^5\text{-}C_5H_5)$ and $(\sigma\text{-}C_2H_5O)_2\text{-}(CH_3)_4C_4B_8H_6$. The known triple-decked complex $1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ was also isolated. The new compounds were isolated by thin-layer and column chromatography and characterized from their ^{11}B and ^1H pulse Fourier transform NMR, IR, and mass spectra. An x-ray structure determination of $\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6$ revealed it to be a distorted icosahedron related to $(CH_3)_4C_4B_8H_8$ with $Co(\eta^5\text{-}C_5H_5)$ replacing an apex BH group.

Introduction

The red metallocarboranes $[(CH_3)_2C_2B_4H_4]_2FeH_2$ and $[(CH_3)_2C_2B_4H_4]_2CoH$ are remarkable chemical species which have been shown to undergo several types of reaction,[1,2] including reversible deprotonation, insertion of $(\eta^5\text{-}C_5H_5)Co$, and, most strikingly, high-yield formation of the tetracarbon carborane $(CH_3)_4C_4B_8H_8$ on exposure of either metallocarborane to the atmosphere.[1-3] The known structure[4] of $(CH_3)_4C_4B_8H_8$, a distorted icosahedron consisting of two $(CH_3)_2C_2B_4H_4$ pyramids joined face-to-face, suggests that it forms by elimination of the FeH_2 or CoH moiety accompanied by oxidative fusion of the two $(CH_3)_2C_2B_4H_4^{2-}$ ligand groups. The face-to-face ligand-fusion phenomenon is thus far unique in boron chemistry, and it has seemed to us increasingly likely that the unusual behavior of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ and $[(CH_3)_2C_2B_4H_4]_2CoH$ is associated with the metal-bound hydrogen atoms, structural features that are absent in other bis-ligand transition-metal carborane complexes. A recent x-ray analysis[5] has confirmed the gross structure proposed earlier[1] for $[(CH_3)_2C_2B_4H_4]_2FeH_2$, except that the carborane ligands are rotated in the solid such that the CCH_3 units are inequivalent with only one cage carbon atom in each ligand "eclipsed" relative to its counterpart in the other ligand. Related crystallographic studies have been conducted on $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$[6] (a product generated by insertion of $(C_5H_5)Co$ into the iron complex), on $(CH_3)_4C_4B_8H_8$ itself,[4] and on several metallocarboranes[7] derived from the latter molecule. At present, our information on the behavior of the metal-bound protons in solution consists of ^1H and ^{11}B NMR data[1,2] which indicate tautomeric exchange through several face-bound locations on the polyhedral surface in the vicinity of the metal.

As part of a continuing investigation of the chemistry of these species, we have extended our earlier study[1] of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ and now present the recent findings.

Results and Discussion

Reaction with Carbon Monoxide. In an earlier report[1] we described the room-temperature interaction of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ under UV light to generate two iron–cobalt metallocarboranes formulated as $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$ and $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_3Fe(CO)_3$, the latter species consisting of a seven-vertex CoC_2B_3Fe polyhedron. The remarkable aspect of the formation of the second compound is the transfer of carbonyl groups from cobalt to iron, with the carbonyls replacing one of the $(CH_3)_2C_2B_4H_4$ carborane ligands in the process. As a follow-up to that observation we have examined the direct thermal reaction of the iron complex with CO gas at low pressure (1.6 atm). The main product, isolated in 76% yield after 4 h at 200 °C, was a bright yellow solid which has been characterized as $(CO)_3Fe(CH_3)_2C_2B_7H_7$ (I) and assigned the structure shown in Figure 1.

The structural characterization of I follows from its ^{11}B and ^1H NMR spectra (Tables I and II) which reveal a 2:2:2:1 pattern of BH groups as well as nonequivalent methyl groups. The molecule is cage-isoelectronic with $B_{10}H_{10}^{2-}$, $C_2B_8H_{10}$, and