pyridine would be lessened by increased steric interaction with the 2-bromo substituent. A similar argument can be given in comparing the relative basicities of 2-chloropyridine and 3-chloropyridine.

It is surprising that only the *cis* adducts were detected by nmr for the 2-halopyridine complexes since it has been shown that both the *cis* and *trans* complexes are formed with 2-methylpyridine 1-oxide and only the *trans* compound is formed with 2,6-dimethylpyridine 1-oxide.[6] The occurrence of *cis–trans* isomerism in $MF_4 \cdot 2(donor)$ depends upon steric effects and $p\pi–d\pi$ bonding.[13] Formation of *trans*-$TiF_4 \cdot 2[2,6-(CH_3)_2-C_5H_3NO]$ was explained on the basis of a steric effect.[6] Since the pyridines are good π acceptors,[14,15] they should increase the ability of the fluorines to π bond to titanium and will stabilize the *cis* complexes. In contrast, a lone pair of electrons on the oxygen of the pyridine 1-oxides will be competing with the fluorines for the titanium π-bonding orbitals.

As indicated previously, most of the titanium tetrafluoride complexes studied have been with monofunctional oxygen donors. Most of these donors are weaker bases (comparison of pK_a values) than the weakest donor listed in Table I. A preliminary reaction of *p*-bromo-N,N-dimethylaniline N-oxide yielded an insoluble adduct which is suggestive of a 1:1 adduct. The basicity of the aniline N-oxide is much greater than that of the pyridine N-oxides. In conclusion it appears that 1:1 complexes are favored by strong bases whereas 2:1 adducts are formed only with weak bases.

Acknowledgment.—Support of this work by the Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson AFB, Ohio, is gratefully acknowledged.

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(14) H. C. A. King, E. Koros, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963).
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The Hydrogen Exchange between Pentaborane-9 and Silane[1a]

By Martin L. Thompson[1b] and Riley Schaeffer

Little attention has been paid to the interaction between hydrides of boron and silicon. This work was attempted to determine whether silane-d_4 and pentaborane-9 would undergo hydrogen atom exchange and, if so, whether the transfer might occur preferentially at

(1) (a) This work was taken from a dissertation submitted by M. L. Thompson in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Indiana University. (b) Department of Chemistry, Lake Forest College, Lake Forest, Ill. 60045.
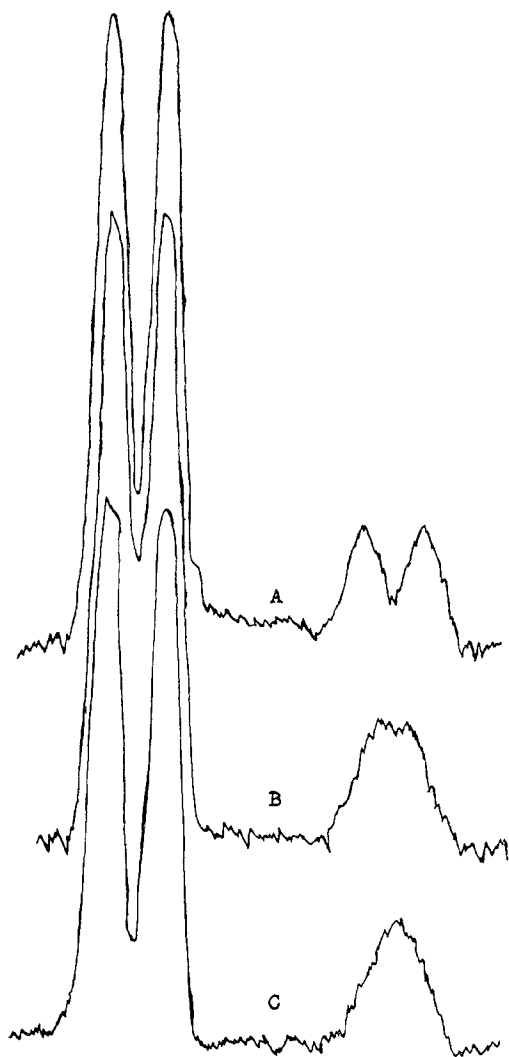
the apical position (believed to be the most susceptible to electrophilic attack[2]) or the basal positions of the latter.

Experimental Section

Apparatus and Equipment.—All chemical reactions were carried out in a vacuum line equipped with mercury-float valves. Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer, Model 137. The samples were confined in a 5-cm gas cell with sodium chloride windows. Boron nmr spectra were obtained at 19.3 Mc/sec with a Varian DP-60 high-resolution spectrometer. Mass spectra were obtained with a Consolidated Engineering Corp. mass spectrometer, Model 21-620.

Chemicals.—Deuterated silane was prepared by a slight modification of the method of Finholt, *et al.*[3] Powdered lithium aluminum deuteride (99.9% D) was slowly dropped into a flask containing a solution of silicon tetrachloride in di-*n*-butyl ether. The silane-d_4 evolved was purified by passage through a $-161°$ trap and its infrared spectrum was identical with that reported previously.[4] Pentaborane-9 (Olin Mathieson Co.) had a vapor pressure of 66 torr at 0° (lit. value 66 torr[5]) and was used without further purification. Deuterium chloride was prepared by the reaction of silicon tetrachloride and deuterium oxide.[6]

Hydrogen Exchange between Pentaborane-9 and Deuterated Silane.—Silane-d_4 (0.28 mmol) and 0.23 mmol of pentaborane-9 were condensed together in a U tube and allowed to equilibrate at room temperature for 10 min. Separation was then achieved by a single passage through a $-161°$ trap. The more volatile silane was recovered quantitatively. An infrared spectrum of this distillate showed the presence of only silane-d_4 indicating that no exchange had occurred. The gases were then mixed together and allowed to remain at room temperature for 17 hr. They were separated as above, and again the infrared spectrum of the silane fraction indicated no evidence of hydrogen transfer.

The gases were then transferred to an all-glass reaction tube equipped with a seal-off and break-off; the tube was sealed and placed in an oven at 125° for 44 hr (total pressure in the tube was 0.45 atm). On opening, no noncondensable gas was observed. The products were separated as above. An infrared spectrum of the distillate confirmed the presence of mixed protonated and deuterated monosilane molecules. The condensate was also sampled for an infrared spectrum and the appearance of the B–D stretching frequency proved that exchange had occurred.

To determine whether proton exchange was selective in the pentaborane molecule, 0.82 mmol of silane-d_4 and 0.37 mmole of pentaborane-9 were placed in an all-glass reaction bulb and allowed to equilibrate for 21 hr at 125°. The total pressure in the bulb was calculated to be 1.2 atm. The gases were separated by a single pass through a $-105°$ trap. The distillate (silane fraction) was sampled for an infrared spectrum and the components were identified as silane-d_4 and silane-d_3.[4] The infrared spectrum of the pentaborane-9 fraction agreed well with that reported by Onak and Williams[7] for pentaborane-9 with a deuterium atom substituted at the apical position. The spectrum is quite similar to that of normal pentaborane-9, the most distinguishing feature being the appearance of a new band at 5.06 μ.

A B^{11} nmr spectrum of the pentaborane-9 fraction was obtained. A comparison between the nmr spectra of the pentaborane-9 obtained from the above reaction and normal pentaborane-9 is shown in Figure 1.

The pentaborane-9 fraction was also sampled for a mass spectrum. The upper region of the spectrum is shown in Table I

(2) B. N. Figgis and R. L. Williams, *Spectrochim. Acta*, **15**, 331 (1959).
(3) A. E. Finholt, A. C. Bond, K. E. Wilzbach, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692 (1947).
(4) J. H. Meal and M. K. Wilson, *J. Chem. Phys.*, **24**, 385 (1956).
(5) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.
(6) G. Bauer, "Handbuch der Preparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, Germany, 1954.
(7) T. P. Onak and R. E. Williams, *Inorg. Chem.*, **1**, 106 (1962).

Figure 1.—B^{11} nmr spectra of pentaborane-9 in carbon disulfide: (A) normal pentaborane-9; (B) pentaborane-9 from $B_5H_9 + SiD_4$ (125° for 21 hr); (C) pentaborane-9 from $B_5H_9 + DCl + Al_2Cl_6$ (25° for 2 hr).

TABLE I

UPPER PORTION OF MASS SPECTRA OF
PARTIALLY DEUTERATED PENTABORANE-9 SPECIES

m/e	B_5H_9	SiD$_4$ + B$_5$H$_9$		DCl + B$_5$H$_9$ + Al$_2$Cl$_6$	
		21 hr at 125°	6 hr at 125°	2 hr at 25°	20 hr at 125°
60	98.5	100.0	100.0	100.0	100.0
61	67.2	86.4	78.4	81.2	85.2
62	70.5	80.0	78.4	75.7	79.1
63	54.8	72.3	66.4	69.8	71.8
64	47.7	63.2	55.4	59.0	61.6
65	...	38.1	20.3	31.8	36.0
66	...	14.7	5.50	1.44	12.8
67	...	3.60	0.94	...	3.81
68	...	...	...	...	1.02
69	...	...	...	...	0.28

borane-9 fraction indicated substitution in at least five positions in this case.

Results and Discussion

Pentaborane-9 and silane-d_4 undergo hydrogen transfer at 125°, as evidenced by the infrared spectra of the resulting silane and pentaborane-9. A mass spectrum of the pentaborane-9 showed that deuterium substitution had occurred to some extent in three positions after equilibration for 6 or 21 hr. The B^{11} nmr spectrum suggests that there was preferential hydrogen exchange at the apical site of the pentaborane molecule, as shown by the nearly complete collapse of the upfield doublet. That exchange has also occurred on the basal borons is indicated by the reduced splitting of the low-field doublet.

The aluminum chloride catalyzed deuteration of pentaborane-9 by deuterium chloride at room temperature was found to be highly predominant at the apical position[7] but not altogether selective, as evidenced by the mass spectrum of the pentaborane product. Under more extreme conditions (20 hr at 125°), at least five positions in the pentaborane molecule were deuterated. Studies of the thermal rearrangement of 1-deuteriopentaborane-9[8] have shown that the lowest temperature at which rearrangement occurred at a satisfactory rate was *ca.* 145° (a minor change was observed in the H^1 nmr spectrum after 20 hr at 135°) and that this was occurring intermolecularly. Thus the reduced splitting of the low-field doublet in the B^{11} nmr spectrum and the polydeuterio substitution indicated by the mass spectrum of pentaborane after exchange with silane-d_4 must be due to direct exchange at positions other than the apex. It cannot be caused by unique apex substitution followed by intra- and/or intermolecular rearrangements of the 1-deuteriopentaborane-9.

Although it is presumptive to speculate on the mechanism of hydrogen transfer, the preference for attack by silane at the apical position of pentaborane-9 can be interpreted as evidence for the weak Lewis acid character of silane. The extent of the deuterium enrichment in pentaborane at 125° is less than that observed under similar conditions when deuterium chlo-

and indicates that deuterium substitution has occurred in at least three positions of the pentaborane molecule.

In another experiment where 0.43 mmol of silane-d_4 and 0.28 mmol of pentaborane-9 were equilibrated at 125° for 6 hr (total pressure 0.76 atm), the upper portion of the mass spectrum of the pentaborane fraction again indicated that substitution has occurred in at least three different positions, but to a lesser degree than previously (see Table I).

Deuterium Exchange of Pentaborane-9 with Deuterium Chloride in the Presence of Aluminum Chloride.—It has been reported that deuterium substitution occurs at the apical position of pentaborane-9 when deuterium chloride is equilibrated with the former over aluminum chloride for 2 hr at room temperature.[7] It was of interest to compare this reported selective deuteration with that obtained in the above experiment. Pentaborane-9 (0.38 mmol) and 0.78 mmol of deuterium chloride were allowed to remain for 2 hr in a flask whose walls were coated with freshly sublimed aluminum chloride. Separation by passage into a −105° trap yielded a pentaborane-9 fraction whose B^{11} nmr spectrum (Figure 1) indicated apical substitution only but whose mass spectrum (Table I) indicated a small amount of disubstitution, as evidenced by a small peak at m/e 66. In another trial similar quantities of deuterium chloride and pentaborane-9 were heated to 125° for 20 hr in an aluminum chloride coated flask. The upper region of the mass spectrum (Table I) of the penta-

(8) T. P. Onak, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **85**, 1754 (1963).

ride in the presence of the electrophilic catalyst, aluminum chloride, is the exchanging moiety. The lack of detectable exchange between pentaborane-9 and silane-d_4 at room temperature indicates a higher activation energy for hydrogen transfer than required for the pentaborane-9–deuterium chloride–aluminum chloride system.

Kinetics of the Thermal Decomposition and Substitution Reactions of Molybdenum Pentacarbonyl Amine Compounds[1]

BY D. J. DARENSBOURG[2] AND THEODORE L. BROWN

Kinetic studies of the substitution reactions of $Mo(CO)_6$ with phosphines and amines indicate that these substitutions proceed by an S_N1 mechanism at low ligand concentrations (less than $0.025\ M$).[3] However at concentrations greater than $0.050\ M$ both first- and second-order kinetics are observed.[4] The rate of the reactions obeys the following rate law, where k_1 and k_2 are described in eq 1 and 2.

$$\text{rate} = [k_1 + k_2(\text{L})][Mo(CO)_6]$$

$$Mo(CO)_6 \xrightarrow{k_1} Mo(CO)_5 + CO \xrightarrow[\text{L}]{\text{rapid}} Mo(CO)_5L \quad (1)$$

$$Mo(CO)_6 + L \xrightarrow{k_2} Mo(CO)_5L + CO \quad (2)$$
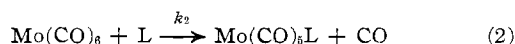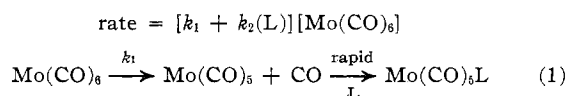
We have found that $Mo(CO)_5C_5H_{10}NH$ and $Mo(CO)_5$-C_5H_5N decompose in solution to give $Mo(CO)_6$ at room temperature. The kinetics for the decomposition of $Mo(CO)_5C_5H_{10}NH$ alone and in the presence of phosphorus ligands have been studied.

Experimental Section

The decomposition reactions were qualitatively followed by observing the disappearance of bands in the CO stretching region of the infrared spectra. Simultaneously the appearance of bands due to $Mo(CO)_6$ or phosphorus-substituted $Mo(CO)_6$ was observed. These measurements were taken at the temperature of the cell compartment of the Beckman IR-7 instrument, which varied from 43 to 46°. The infrared spectra were employed only for product identification and concentration.

Quantitative rate data for both decomposition and substitution were obtained on a Cary Model 15 by observing the disappearance of the characteristic band at 397.5 mμ in the visible spectrum of

(1) This research was supported in part by a grant from the National Science Foundation.
(2) National Institutes of Health Predoctoral Fellow, 1967–1968.
(3) H. Werner, *J. Organometal. Chem.* (Amsterdam), **5**, 100 (1966).
(4) R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **88**, 3658 (1966).

$C_5H_{10}NHMo(CO)_5$. Constant temperature was maintained by means of a close-fitting brass block mounted in the cell compartment. The temperature of the block was maintained by a flow of thermostated water through internal holes and was measured by means of an NBS Certified thermometer.

The complexes were prepared as previously described.[5] Solvents were spectral grade hexane or carbon disulfide, used without further treatment.

Linear first-order plots of ln $(A - A_\infty)$, where A is the absorbance at time t and A_∞ is the absorbance at infinite time, *vs.* t were obtained. These plots were linear for at least 75% reaction completion. All data were subjected to a least-squares treatment.
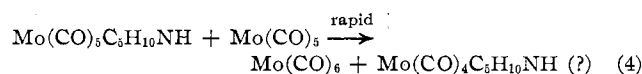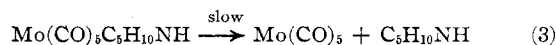
Results and Discussion

The quantities of $Mo(CO)_6$ present upon completion of three kinetic runs involving $Mo(CO)_5C_5H_{10}NH$ in carbon disulfide, at concentrations of 2.056, 3.029, and $3.627 \times 10^{-4}\ M$, represented 48.6, 49.5, and 50.8%, respectively, of the starting material. Rate constants for the decomposition reaction in both hexane and carbon disulfide solvents at various temperatures are listed in Table I.

TABLE I
FIRST-ORDER RATE CONSTANTS FOR THE DISSOCIATION
OF $Mo(CO)_5C_5H_{10}NH$

In hexane		In carbon disulfide	
Temp, °C	10^5k_1, sec^{-1}	Temp, °C	10^5k_1, sec^{-1}
33.5	1.49	33.5	7.27
39.6	3.17	39.9	15.40
40.0	3.15	49.7	39.60
43.4	4.80		
49.8	10.48		

No quantitative rate data were obtained for the decomposition of $Mo(CO)_5C_5H_5N$ to $Mo(CO)_6$, but qualitatively the reaction was observed from the infrared studies to proceed at a slightly faster rate than for $Mo(CO)_5C_5H_{10}NH$.

We propose that the decomposition proceeds *via* a rate-determining dissociation, analogous to reaction 1 for the substitution reactions

$$Mo(CO)_5C_5H_{10}NH \xrightarrow{\text{slow}} Mo(CO)_5 + C_5H_{10}NH \quad (3)$$

$$Mo(CO)_5C_5H_{10}NH + Mo(CO)_5 \xrightarrow{\text{rapid}}$$
$$Mo(CO)_6 + Mo(CO)_4C_5H_{10}NH \ (?) \quad (4)$$

No evidence for the presence of $Mo(CO)_4[C_5H_{10}NH]_2$ was obtained from the infrared spectra. Since the yield of $Mo(CO)_6$ upon completion of the decomposition reaction is 50%, it appears that the product of a CO abstraction, $Mo(CO)_4[C_5H_{10}NH]$, is not stable and rapidly decomposes to insoluble, metal-containing material. A precipitate is seen upon completion of the reaction, but no attempts were made at identification. Addition of excess piperidine stabilizes the $Mo(CO)_5$-$C_5H_{10}NH$ species. For example, the presence of 0.08 M piperidine results in no measurable production of $Mo(CO)_6$ after several hours.

Addition to the reaction mixture of a second metal carbonyl compound, $Co(CO)_4SiCl_3$, stable with respect to thermal decomposition under the reaction conditions,

(5) D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 959 (1968).