Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Reaction of Dimethyl Sulfide–Triborane(7) with Trimethylamine. Facile Formation of Bis(trimethylamine)–Diborane(4)

Minoru Ishii† and Goji Kodama*

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In 1985, the isolation of once elusive bis(trimethylamin)–diborane(4) was reported from this laboratory.[1] The compound was prepared by the reaction of B_3H_7·THF with excess trimethylamine in tetrahydrofuran. The trimethylamine adduct of B_3H_7, which was produced first by the displacement of tetrahydrofuran, reacted further with $N(CH_3)_3$ at room temperature to form B_2H_4·$2N(CH_3)_3$ and BH_3·$N(CH_3)_3$. Since $S(CH_3)_2$ is a relatively weak Lewis base, dimethyl sulfide–triborane(7) [B_3H_7·$S(CH_3)_2$] was expected to undergo a reaction with $N(CH_3)_3$ in a manner similar to that observed for B_3H_7·THF. Indeed, the treatment of B_3H_7·$S(CH_3)_2$ with $N(CH_3)_3$ gave B_2H_4·$2N(CH_3)_3$ and BH_3·$N(CH_3)_3$. However, this reaction appeared to give the products at much lower temperatures than the B_3H_7·THF reaction did. Therefore, we decided to take a closer look at these two reactions by monitoring the reaction progresses with NMR spectroscopy.

Results

Dimethyl sulfide–triborane(7) reacted with trimethylamine in dimethyl sulfide, slowly at −80 °C and rapidly at −30 °C, to form B_2H_4·$2N(CH_3)_3$ and BH_3·$N(CH_3)_3$. This observation is summarized by eq 1. During the initial stage of this reaction, a very

$$B_3H_7{\cdot}S(CH_3)_2 + 3N(CH_3)_3 \xrightarrow[\text{in } S(CH_3)_2]{-80 \text{ to } -30\ ^\circ C} B_2H_4{\cdot}2N(CH_3)_3 + BH_3{\cdot}N(CH_3)_3 \quad (1)$$

small amount of B_3H_7·$N(CH_3)_3$ was produced in the solution. This B_3H_7·$N(CH_3)_3$ disappeared eventually as the solution was allowed to warm to room temperature.

The above reaction of B_3H_7·$S(CH_3)_2$ with $N(CH_3)_3$ to form B_2H_4·$2N(CH_3)_3$ contrasted with that of B_3H_7·THF with $N(CH_3)_3$ to form the same product. When B_3H_7·THF was treated with trimethylamine in tetrahydrofuran, a displacement reaction occurred to form B_3H_7·$N(CH_3)_3$, slowly at −80 °C and rapidly at −50 °C. When the temperature was increased to −30 °C, the displacement was completed. As the reaction mixture was allowed to warm to 0 °C, B_2H_4·$2N(CH_3)_3$ and BH_3·$N(CH_3)_3$ began to form slowly, and the reaction was almost complete within 1.5 h at this temperature. These reactions are summarized by eqs 2 and 3. This reaction of B_3H_7·THF with $N(CH_3)_3$ to form

$$B_3H_7{\cdot}THF + N(CH_3)_3 \xrightarrow[\text{in THF}]{-80 \text{ to } -30\ ^\circ C} B_3H_7{\cdot}N(CH_3)_3 + THF \quad (2)$$

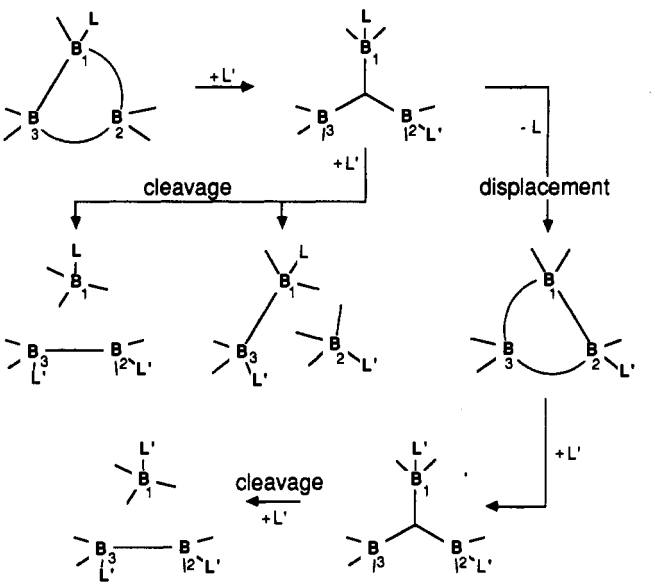
$$B_3H_7{\cdot}N(CH_3)_3 + 2N(CH_3)_3 \xrightarrow[\text{in THF}]{0\ ^\circ C \text{ or above}} B_2H_4{\cdot}2N(CH_3)_3 + BH_3{\cdot}N(CH_3)_3 \quad (3)$$

B_2H_4·$2N(CH_3)_3$ has already been reported.[1] In this study, however, the reaction was performed under conditions that were comparable with those employed for the B_3H_7·$S(CH_3)_2$ reaction described above. Clearly, B_2H_4·$2N(CH_3)_3$ was produced more readily, or at a lower temperature, from B_3H_7·$S(CH_3)_2$ than it was from B_3H_7·THF.

When B_3H_7·$S(CH_3)_2$ was treated with excess $N(CH_3)_3$ (a 1:4 molar ratio) in dichloromethane, the B_2H_4·$2N(CH_3)_3$ formation was complete *within several minutes at −80 °C*. Once B_3H_7·$N(CH_3)_3$ had been formed as a side product at the low temperature, the cleavage of the B_3H_7·$N(CH_3)_3$ did not occur until a higher temperature was reached. This point was substantiated by a separate experiment in which B_3H_7·$N(CH_3)_3$ was treated with $N(CH_3)_3$ in $S(CH_3)_2$.

When B_3H_7·$S(CH_3)_2$ was treated with a deficient amount of $N(CH_3)_3$ (a 1:2 molar ratio) in dichloromethane or $S(CH_3)_2$, the formation of B_2H_4·$2N(CH_3)_3$ occurred at the low temperature in a manner similar to that described above. The excess B_3H_7·$S(CH_3)_2$ remained unchanged until it began to react with B_2H_4·$2N(CH_3)_3$ to form B_4H_8·$N(CH_3)_3$ at a higher temperature.[2]

Scheme I



Discussion

Reactions of Lewis base (L) adducts of triborane(7), B_3H_7·L, with second Lewis bases (L′) have been thought to proceed through the formation of an intermediate, B_3H_7·L·L′.[3-5] As illustrated in Scheme I, the intermediate undergoes two different types of reactions depending upon the nature of the two basees, L and L′: (1) the elimination of L from the intermediate results in a displacement reaction and (2) the reaction of the intermediate with another L′ gives the cleavage products B_2H_4·L·L′ + BH_3·L′ or the products B_2H_4·2L′ + BH_3·L. When L is a weak base and L′ is a "stronger" base, the displacement reaction is usually observed. Several examples of this type of reaction are given by eqs 4–7.

$$B_3H_7{\cdot}THF + NH_{3-n}(CH_3)_n \rightarrow B_3H_7{\cdot}NH_{3-n}(CH_3)_n + THF \quad (n = 0\text{–}3)^6 \quad (4)$$

$$B_3H_7{\cdot}THF + PH_{3-n}(CH_3)_n \rightarrow B_3H_7{\cdot}PH_{3-n}(CH_3)_n + THF \quad (n = 0\text{–}3)^7 \quad (5)$$

$$B_3H_7{\cdot}O(CH_3)_2 + PF_2H \rightarrow B_3H_7{\cdot}PF_2H + O(CH_3)_2{}^8 \quad (6)$$

$$B_3H_7{\cdot}THF + S(CH_3)_2 \rightarrow B_3H_7{\cdot}S(CH_3)_2 + THF^2 \quad (7)$$

These displacement reactions usually occur at lower temperatures when the attacking base is strong. For example, as described under Results, the displacement of tetrahydrofuran by $N(CH_3)_3$ occurred at −80 °C. Since $S(CH_3)_2$ is a base that is considerably weaker than $N(CH_3)_3$, one might have predicted that $N(CH_3)_3$ would displace $S(CH_3)_2$ from B_3H_7·$S(CH_3)_2$ to form B_3H_7·$N(CH_3)_3$ first. The experimental result showed that it was not the case.

When L and L′ are both relatively strong bases, or both relatively weak bases, the cleavage reaction occurs as shown in eqs 8–11. Due to the inductive effect of the base that is bonded to

* To whom correspondence should be addressed.
† Present address: Chemistry Laboratory, Department of Education, Yamagata University, 1-4-12 Koshirakawa, Yamagata 990, Japan.

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$$B_3H_7{\cdot}N(CH_3)_3 + 2N(CH_3)_3 \rightarrow B_2H_4{\cdot}2N(CH_3)_3 + BH_3{\cdot}N(CH_3)_3$$[1] (8)

$$B_3H_7{\cdot}N(CH_3)_3 + 2P(CH_3)_3 \rightarrow B_2H_4{\cdot}2P(CH_3)_3 + BH_3{\cdot}N(CH_3)_3$$[5] (9)

$$B_3H_7{\cdot}P(CH_3)_3 + 2N(CH_3)_3 \rightarrow B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3 + BH_3{\cdot}N(CH_3)_3$$[5] (10)

$$B_3H_7{\cdot}PF_2X + 2PF_2X \rightarrow B_2H_4{\cdot}2PF_2X + BH_3{\cdot}PF_2X \quad (X = H,^8 F, Cl, Br^4)$$ (11)

the B_3H_7 fragment, a strong-base adduct of B_3H_7 acts as a weak borane acid and, conversely, a weak-base adduct of B_3H_7 behaves as a strong acid; i.e., the B_2 and B_3 sites (Scheme I) of the strong-base adduct are less reactive toward nucleophiles than the corresponding sites in the weak-base adduct. Consequently, a strong base is required for a strong-base adduct of B_3H_7 to form the intermediate and to give the cleavage products (eqs 8–10). On the other hand, the weak-base adduct can react even with a weak base to form the intermediate for the cleavage reaction (eq 11). These cleavage reactions listed above proceed slowly at higher temperatures (ca. −30 to 0 °C).

Since $S(CH_3)_2$ is a relatively weak base, $B_3H_7{\cdot}S(CH_3)_2$ is expected to behave as a relatively strong acid. Therefore, $B_3H_7{\cdot}S(CH_3)_2$ would form the intermediate with $N(CH_3)_3$ more readily than $B_3H_7{\cdot}N(CH_3)_3$ would. The same consideration applies to the reactivity of the intermediate toward $N(CH_3)_3$; i.e., the $S(CH_3)_2$-containing intermediate is expected to react readily with the strong attacking base, $N(CH_3)_3$. According to the model shown in Scheme I, the resulting cleavage products would be either $B_2H_4{\cdot}2N(CH_3)_3 + BH_3{\cdot}S(CH_3)_2$ or "$B_2H_4{\cdot}S(CH_3)_2{\cdot}N(CH_3)_3$" + $BH_3{\cdot}N(CH_3)_3$. Currently, no evidence is available to identify this cleavage pathway. The dimethyl sulfide in $BH_3{\cdot}S(CH_3)_2$ is known to be readily displaced by $N(CH_3)_3$,[9] and by the same token, "$B_2H_4{\cdot}S(CH_3)_2{\cdot}N(CH_3)_3$" is thought to undergo a facile displacement reaction with $N(CH_3)_3$ to form $B_2H_4{\cdot}2N(CH_3)_3$ at the low temperature. Thus, the facile cleavage of $B_3H_7{\cdot}S(CH_3)_2$ by $N(CH_3)_3$ appears to be the result of having a relatively weak base bonded to the B_3H_7 fragment and a strong base attacking the adduct.

The observed fast, facile cleavage of $B_3H_7{\cdot}S(CH_3)_2$ by $N(CH_3)_3$, in particular the reaction with excess $N(CH_3)_3$ in CH_2Cl_2, should be able to be used as an alternative and practical method for the preparation of $B_2H_4{\cdot}2N(CH_3)_3$. Furthermore, this low-temperature formation of the B_2H_4 adduct suggested an attractive route for preparing the B_2H_4 adducts of secondary and primary amines. Unfortunately, our preliminary study on the reaction of $B_3H_7{\cdot}S(CH_3)_2$ with $NH(CH_3)_2$ indicated that, although the reaction occurred at low temperatures and $BH_3{\cdot}N(CH_3)_2H$ was produced, the B_2H_4 moiety was ruptured by the amine to finally form $HB[N(CH_3)_2]_2$. The results of this reaction study on the series of amines will be reported at a future date.

Experimental Section

Chemicals and Equipment. Conventional vacuum-line techniques were used throughout for the handling of the volatile compounds. Tetraborane(10) was prepared from $[(CH_3)_4N]B_3H_8$ (Alfa Products) by the literature method.[10] Trimethylamine (Kodak Laboratory and Research Product) was refluxed and distilled over CaH_2 and then stored in a steel cylinder. Commercial tetrahydrofuran and dimethyl sulfide were refluxed and distilled over lithium aluminum hydride and calcium hydride, respectively, and stored over molecular sieves. These liquids were distilled from their storage containers directly into the vacuum line as needed. The ^{11}B NMR spectra were obtained on a Varian XL-300 spectrometer which was equipped with a probe that can accommodate a 16 mm o.d. sample tube. The solutions for spectrum recording were clear and colorless unless stated otherwise. Compounds were identified by their ^{11}B NMR chemical shifts. These shift values are available in the respective references cited: $B_3H_7{\cdot}S(CH_3)_2$,[2] $B_3H_7{\cdot}N(CH_3)_3$,[6] $B_2H_4{\cdot}2N(CH_3)_3$,[1] $BH_3{\cdot}S(CH_3)_2$,[11a] $BH_3{\cdot}N(CH_3)_3$,[11b] $B_4H_8{\cdot}S(CH_3)_2$,[12] and $B_4H_8{\cdot}N(CH_3)_3$.[9]

Reaction of $B_3H_7{\cdot}S(CH_3)_2$ with $N(CH_3)_3$ in $S(CH_3)_2$. (a) $N(CH_3)_3$ in an Excess Amount. A sample of $B_3H_7{\cdot}THF$ was prepared from a 0.42-mmol sample of B_4H_{10}[13] in a 14 mm o.d. Pyrex tube equipped with a vertical-shape Teflon valve (VNMR value, product of J. Young Scientific Glassware), and about 3 mL of $S(CH_3)_2$ was condensed into the tube to convert the $B_3H_7{\cdot}THF$ into $B_3H_7{\cdot}S(CH_3)_2$.[2] Then, a 2.03-mmol sample of $N(CH_3)_3$ was condensed into the tube. The mixture was agitated at −95 °C for thorough mixing, and the tube was inserted into the probe of the NMR spectrometer. The ^{11}B spectra were recorded from −80 to +20 °C during a total period of about 1 h, the temperature being increased in increments of 10–20 °C. At −80 °C, $B_2H_4{\cdot}2N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$ were forming slowly. Above −70 °C, the formation of these compounds was fast and the $B_3H_7{\cdot}S(CH_3)_2$ was rapidly consumed. A small amount of $B_3H_7{\cdot}N(CH_3)_3$ was seen at −80 °C and persisted until the temperature reached −10 °C, at which it began to disappear.

(b) $N(CH_3)_3$ in a Deficient Amount. A 0.492-mmol sample of $B_3H_7{\cdot}S(CH_3)_2$ was weighed[2] into a 10 mm o.d. Pyrex tube and was treated with a 0.974-mmol sample of $N(CH_3)_3$ in 9.87 mmol of $S(CH_3)_2$. In this experiment, the $N(CH_3)_3$ was slowly added to the tube, which was held in a −95 °C bath. At −95 to −80 °C, $B_2H_4{\cdot}2N(CH_3)_3$, $BH_3{\cdot}N(CH_3)_3$, $B_3H_7{\cdot}S(CH_3)_2$, and a small amount of $B_3H_7{\cdot}N(CH_3)_3$ were present in the solution. As the temperature was raised slowly, the $B_2H_4{\cdot}2N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$ signals gained intensities rapidly, and at −20 °C signals of $B_4H_8{\cdot}N(CH_3)_3$ appeared. The temperature was then raised to 20 °C, and the solution was held at that temperature for 30 min; during this time the intensities of the $B_4H_8{\cdot}N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$ signals increased and those of the $B_2H_4{\cdot}2N(CH_3)_3$ and $B_3H_7{\cdot}S(CH_3)_2$ signals decreased.

Reaction of $B_3H_7{\cdot}THF$ with $N(CH_3)_3$ in Tetrahydrofuran. A sample of $B_3H_7{\cdot}THF$ was prepared from 0.52 mmol of B_4H_{10} in a 14 mm o.d. Pyrex tube and was dissolved in about 2.5 mL of tetrahydrofuran. The solution was then frozen at −197 °C, and a 2.91-mmol sample of $N(CH_3)_3$ was condensed into the tube. The tube was then shaken in a −95 to −80 °C bath and placed in the probe for recording of the ^{11}B NMR spectra in the manner similar to that described above for the $B_3H_7{\cdot}S(CH_3)_2$ reaction. At −80 °C, $B_3H_7{\cdot}N(CH_3)_3$ was forming slowly. The formation of $B_3H_7{\cdot}N(CH_3)_3$ was rapid at −50 °C, and as the temperature was raised to −30 °C, $B_3H_7{\cdot}THF$ was almost gone. At 0 °C, the signal of $B_2H_4{\cdot}2N(CH_3)_3$ began to appear slowly. The intensities of the $B_2H_4{\cdot}2N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$ signals increased considerably during the 30-min holding time at this temperature, but the $B_3H_7{\cdot}N(CH_3)_3$ signal intensity was still strong. An additional time period of 60 min was required for the $B_3H_7{\cdot}N(CH_3)_3$ signal to disappear completely.

Reaction of $B_3H_7{\cdot}S(CH_3)_2$ with $N(CH_3)_3$ in CH_2Cl_2. (a) $N(CH_3)_3$ in an Excess Amount. A sample of $B_3H_7{\cdot}S(CH_3)_2$ was prepared in a 9 mm o.d. Pyrex tube from a 0.49-mmol sample of B_4H_{10} and was dissolved in about 2 mL of CH_2Cl_2. Then, the solution was frozen at −197 °C, and a 2.03-mmol sample of $N(CH_3)_3$ was condensed into the tube. The mixture was shaken in a −80 °C bath, and then the tube was placed in the probe of the NMR spectrometer. At −75 °C, $B_3H_7{\cdot}S(CH_3)_2$ was no longer present and the formation of $B_2H_4{\cdot}2N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$ had been completed.

(b) $N(CH_3)_3$ in a Deficient Amount. In another experiment, a 0.30-mmol sample of $B_3H_7{\cdot}S(CH_3)_2$ was weighed into a 10 mm o.d. Pyrex tube and was dissolved in about 2.5 mL of CH_2Cl_2. A 0.60-mmol sample of $N(CH_3)_3$ (a 1:2 molar ratio) was condensed into the tube, and the mixture was shaken in a −80 °C bath before it was placed in the probe of the spectrometer. At −40 °C, in addition to the signals of $B_3H_7{\cdot}S(CH_3)_2$, $B_2H_4{\cdot}2N(CH_3)_3$, and $BH_3{\cdot}N(CH_3)_3$, weak signals of $B_4H_8{\cdot}N(CH_3)_3$ were clearly detectable. As the temperature was raised to −20 °C, the intensities of the $B_4H_8{\cdot}N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$ signals increased at the expense of the $B_3H_7{\cdot}S(CH_3)_2$ and $B_2H_4{\cdot}2N(CH_3)_3$ signal intensities. A trace quantity of $B_3H_7{\cdot}N(CH_3)_3$ was found in the solution.

Reaction of $B_3H_7{\cdot}N(CH_3)_3$ with $N(CH_3)_3$ in $S(CH_3)_2$. A 0.31-mmol sample of $B_3H_7{\cdot}N(CH_3)_3$[7] was weighed into a 10 mm o.d. Pyrex tube equipped with a Teflon valve and was dissolved in a 10-mmol sample of $S(CH_3)_2$ at −80 °C. The tube was then placed in a −95 °C bath, a 0.279-mmol sample of $N(CH_3)_3$ was slowly introduced into the tube while the solution was agitated constantly, and then the tube was placed in the probe of the spectrometer. At −80 °C, no change was observed. At −40 °C, the signals of $B_2H_4{\cdot}2N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$ were barely detectable. As the temperature was raised first to −20 °C and then to 0 °C intensities of the $B_2H_4{\cdot}2N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$ signals increased rapidly. (The rate increase coincided with the disappearance of

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a crystalline precipitate of presumably $B_3H_7{\cdot}N(CH_3)_3$.) The intensity ratio for $B_2H_4{\cdot}2N(CH_3)_3$:$BH_3{\cdot}N(CH_3)_3$ remained 2:1. When the solution was allowed to staad at room temperature for 2.5 h, the signals of $B_4H_8{\cdot}N(CH_3)_3$ had grown in the spectrum and the intensity of the $BH_3{\cdot}N(CH_3)_3$ signal had become greater than that of the $B_2H_4{\cdot}2N(CH_3)_3$ signal. The signal of $B_3H_7{\cdot}N(CH_3)_3$ still remained strong in the spectrum.

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Supplementary Material Available: Two series of spectra for the reaction solutions of $B_3H_7{\cdot}S(CH_3)_2$ + $N(CH_3)_3$ in $S(CH_3)_2$ and of $B_3H_7{\cdot}THF$ + $N(CH_3)_3$ in THF (2 pages). Ordering information is given on any current masthead page.

Contribution from the Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, Japan, and Department of Chemistry, Gorlaeus Laboratories, Leiden University, 2300 RA Leiden, The Netherlands

Unusual Isomerization Reaction of a Platinum–Dinucleotide Compound

Kenji Inagaki,*[1a] Maarten Alink,[1a] Akinori Nagai,[1a] Yoshinori Kidani,*[1a] and Jan Reedijk[1b]

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It has been generally believed that bifunctional attack of antitumor platinum complex, e.g., *cis*-$Pt(NH_3)_2Cl_2$, on DNA is responsible for an appearance of the biological activities.[2] Much attention has been focused on characterization of platinum–oligonucleotide adducts[3] formed after chelation due to *cis*-$Pt(NH_3)_2Cl_2$. The reaction between a bifunctional platinum complex and nucleic acid base occurs via a two-step mechanism,[4] and the first step is normally a preferential binding to the N7 site of a guanine.[5] The present paper mainly describes results obtained about the second step, i.e., chelation after the first platinum binding. The reaction of $[Pt(R,R\text{-dach})(OH_2)_2]^{2+}$ with r(GpA) (abbreviations: *R,R*-dach, 1*R*,2*R*-cyclohexanediamine; r(GpA), guanylyl(3′-5′)adenosine) results in interbase cross-linked compounds between the guanine and the adenine bases. These chelate compounds are formed via the 1:1 aqua intermediate, Pt(*R,R*-dach)(OH_2)(r(GpA)-*N7(1)*). This process is a normal two-step reaction. An intriguing observation is that one of the chelate compounds, which is likely to be a kinetically preferred species, isomerizes very slowly to give the end products. That is, the isomerization process is a reaction in which the kinetically preferred species is slowly converted to thermodynamically more stable chelates. The aim of the present paper is to introduce such an unusual isomerization reaction. Such an isomerization reaction could not be observed in the case of reaction between r(ApG) and $[Pt(R,R\text{-dach})(OH_2)_2]^{2+}$.

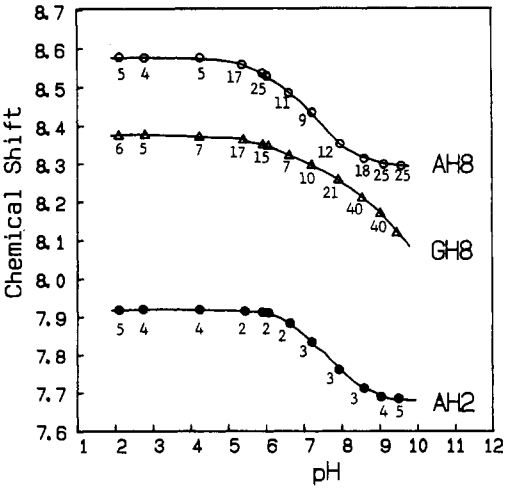

Figure 1. Chemical shift vs pH of the purine base protons of the Pt adduct **4**, Pt(*R,R*-dach)(r(GpA)-*N7(1),N1(2)*). The numbers along the plots indicate the line widths of the signals at half-height (Hz).

The reaction of $[Pt(R,R\text{-dach})(OH_2)_2]^{2+}$ with r(GpA) was followed by means of HPLC as a function of time (10 °C, pH 4.4). The reaction results in four Pt adducts (**1–4**)[6] formed via an aqua 1:1 intermediate. The reaction of Pt(*R,R*-dach)Cl_2 with r(GpA) also results in the same four Pt adducts, in this case without an observable intermediate because the hydrolysis reaction of the dichloro complex is the rate-determining step. The relative ratio of the four Pt adducts was found to be constant throughout the reaction[7] because the isomerization under consideration is very slow at 10 °C. With the reaction at higher temperature, e.g. 37 °C, the relative ratio was almost constant for the first 10 h (see Table I). However, the amount of Pt adduct **4** appeared to decrease thereafter, apparently because of an isomerization reaction. The kinetic parameters obtained under the pseudo-first-order conditions [the concentrations of $[Pt(R,R\text{-dach})(OH_2)_2]^{2+}$ were 10–40 times in excess over those of r(GpA)] are indicated in Table I. The occurring reaction can be described according to the following scheme:

$$\text{r(GpA)} + \text{Pt}(R,R\text{-dach}) \xrightarrow[k_1]{} \text{1:1 aqua intermediate} \xrightarrow[k_c]{} \textbf{1–4} \quad (1)$$

where $k_c = k_{1c} + k_{2c} + k_{3c} + k_{4c}$. Each kinetic constant has been calculated from the relative peak areas of HPLC chromatograms. The kinetic parameters (k_1 and k_c) are in fair agreement with the corresponding parameters reported by Chottard et al.[8] for the reaction between $[cis\text{-}Pt(NH_3)_2(OH_2)_2]^{2+}$ and r(GpA).

In the Pt adducts **2–4**, the binding ratio of $[Pt(R,R\text{-dach})]^{2+}$ to r(GpA) was found to be 1:1, i.e., Pt(*R,R*-dach)(r(GpA)), being calculated from integrations of the H1′ protons of the r(GpA) moiety and the CH protons of the cyclohexane ring in the NMR spectra. Adduct **3** can definitely be assigned to Pt(*R,R*-dach)(r(GpA)-*N7(1),N7(2)*) from evidence of UV, CD (data not

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(7) The relative ratios were calculated from peak areas of the HPLC chromatogram. Although the molar extinction coefficients (at 260 nm) of the Pt adducts and unreacted r(GpA) are not identical, they are expected to be almost the same (Inagaki, K.; Tomita, A.; Kidani, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2825).
(8) These authors[4c] followed the reaction between r(GpA) and $[cis\text{-}Pt(NH_3)_2(OH_2)_2]^{2+}$ by means of UV spectrometry and HPLC and obtained the values $k_1 = 0.8\ M^{-1}\ s^{-1}$ and $k_c = 4.5 \times 10^{-4}\ s^{-1}$ at 20 °C, pH = 5.2. They isolated *cis*-$Pt(NH_3)_2$(r(GpA)-*N7(1),N7(2)*) (68%) and *cis*-$Pt(NH_3)_2$(r(GpA)-*N7(1),N1(2)*) (32%), and the latter compound corresponds to the adduct **4** in this work.

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