

Figure 3. Minimum energy reaction profile (MERP) for the reaction of $\text{BH}_3 + \text{B}_3\text{H}_7$ to form structure 1 or 2. The transition state 5 is 3.1 kcal/mol higher in energy than 6 at the MP2/6-31G* level.

hydrogen that is underestimated at the 3-21G level.⁶ The structure in Figure 2d was completely optimized subject to the constraint that the two forming bridge interactions are 1.70 Å from the more distant boron.⁷ The constraint is not necessary if geometries are optimized at the MP2/3-21G level, as shown recently⁶ for the reaction $\text{B}_3\text{H}_9 \rightarrow \text{B}_2\text{H}_6 + \text{BH}_3$. For that reaction the geometry from the constrained optimization leads to an energy only 1 kcal/mol higher than that of the fully optimized MP2/3-21G geometry when both were calculated at a higher level of theory.⁶ The lowest pathway for decomposition of 2 is not to $\text{B}_3\text{H}_7 + \text{BH}_3$ but rather to $\text{B}_4\text{H}_8 + \text{H}_2$, which has an experimental activation barrier of 24 kcal/mol.^{8,9} Thus, the bis(diboranyl) structure is not likely formed in a direct conversion but could be formed from B_3H_7 and BH_3 , which are present in steady-state concentrations from other pyrolytic reactions. The minimum energy reaction profile (MERP) is shown in Figure 3 for reaction of $\text{B}_3\text{H}_7 + \text{BH}_3$ to form 1 and 2 over transition states 5 and 6, respectively. The reaction to form 1 proceeds with a 2.2 kcal/mol barrier while the reaction to form 2 proceeds with a negative enthalpic barrier (-0.9 kcal/mol).¹⁰

During pyrolysis of diborane (100–150 °C), the product ratio should be determined by the difference in activation barriers corresponding to the two paths for reaction of $\text{B}_3\text{H}_7 + \text{BH}_3$ (3.1 kcal/mol) if under kinetic control, while the ratio should be determined by the difference in stabilities of products (9.0 kcal/mol) if under thermodynamic control. It should be considered that although the barriers for reaction of $\text{B}_3\text{H}_7 + \text{BH}_3$ are low, the concentrations of the two transient boron hydrides will be very small. More likely, the reaction will be between B_3H_7 and a stable boron hydride such as B_2H_6 , where the borane is delivered bound as the dimer. The mechanism of reaction, however, will be unchanged, and the difference in activation barriers will be similar even though the barriers themselves will be higher.⁶

The product ratio (2:1) can be estimated by determining the ratio of rates for the two reactions. The entropy of activation (which is required to compute the A factor) for the reaction $\text{BH}_3 + \text{B}_3\text{H}_7 \rightarrow 2$ can be estimated as the entropy of activation for a closely related reaction, $\text{BH}_3 + \text{B}_2\text{H}_6 \rightarrow \text{B}_3\text{H}_9$, which is $-28.4 \text{ cal deg}^{-1} \text{ mol}^{-1}$ at the MP2/STO-3G level.⁶ For the reaction $\text{BH}_3 + \text{B}_3\text{H}_7 \rightarrow 1$, the entropy of activation is calculated by using the 3-21G vibrational frequencies for the reactants and the transition state ($-29.6 \text{ cal deg}^{-1} \text{ mol}^{-1}$). The entropies of activation for both reactions are negative, which is reasonable for a bimolecular reaction, and similar in magnitude. Calculation of rates using the above approximations leads to a 100:1 product ratio at 100 °C. If the reaction is under thermodynamic control, the ratio would be much greater, 10⁶:1. However, the high reverse barriers (32.6 and 39.4 kcal/mol) should slow the approach to equilibrium concentrations.

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 (10) At the 3-21G level the activation barrier is 15.2 kcal/mol; however, inclusion of correlation and polarization stabilizes the transition state (6) more than $\text{BH}_3 + \text{B}_3\text{H}_7$ resulting in a negative barrier at the MP2/6-31G* level. Since the entropy of activation will be negative for a recombination reaction, the free energy of activation will probably be positive.

Thus, it may be possible to use IR spectroscopy to detect bis(diboranyl) as a minor component under pyrolysis conditions that favor B_4H_{10} formation. It is suggested to look for the asymmetric bridge stretching frequencies, which are predicted to be about 300 cm^{-1} lower in 2 compared to 1. The calculated asymmetric BHB stretches in the "butterfly" structure (2) are 1378, 1514, 1584, and 1611 cm^{-1} (obsd 1308, 1324, 1388, and 1444 cm^{-1})¹¹ compared to 1748, 1826, 1861, and 1878 cm^{-1} in the bis(diboranyl) structure (1) at the 3-21G level. At the same level of computation the calculated asymmetric bridge stretches in B_2H_6 are 1820 and 1915 cm^{-1} (obsd 1602 and 1768 cm^{-1}).¹²

There are two relevant reactions that may actually go through 1 while yielding only 2 as an observable product. In one, mercury-sensitized photolysis of diborane yielded B_4H_{10} in good yield.¹³ Initial formation of B_2H_5^* (9) could form 1 with sufficient excess energy (102.2 kcal/mol) to rearrange to 2. The second reaction, carried out in the early days of boron chemistry by Stock,^{14,15} involved the conversion of $\text{B}_2\text{H}_5\text{I}$ in the presence of sodium amalgam to B_4H_{10} in low yields using a Wurtz-type coupling reaction.¹⁶

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Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Formation of a Binuclear Complex by Reaction of $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$ with Mercury(II)

Margaret J. Sisley and Robert B. Jordan*

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The carbon-chromium bond in organochromium complexes of the type $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ is cleaved readily by electrophiles such as mercury(II). The rate constants for a large number of these reactions with Hg^{2+} and varying $-\text{R}$ groups have been determined.¹ There have been two kinetic studies of reaction 1 which confirmed $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+} + \text{Hg}^{2+} + \text{H}_2\text{O} \rightarrow$



the rate law given in eq 2. There is satisfactory agreement on

$$\text{rate} = k_{\text{Hg}}[\text{CrCH}_2\text{CN}^{2+}][\text{Hg}^{2+}] \quad (2)$$

the value of k_{Hg} of 9.8² and 8.7³ $\text{M}^{-1} \text{s}^{-1}$ (25 °C, 1 M $\text{LiClO}_4/\text{HClO}_4$).

In this note it is shown that eq 1 is not a complete representation of the reaction in that the true products are not just those shown. The present observations have implications for other such reactions, especially if the organic group has substituents that can coordinate to chromium(III).

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Table I. Electronic Spectral Properties of Chromium(III) Species

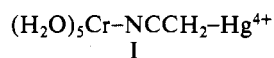
species	electronic spectra	
	λ_{\max} , nm (ϵ , $M^{-1} \text{ cm}^{-1}$)	
$(\text{H}_2\text{O})_5\text{CrNCCH}_2\text{Hg}^{4+}$	563 (21.0)	398 (25.9)
$(\text{H}_2\text{O})_5\text{CrNCCH}_3^{3+}$	566 (15.7) ^a	397 (21.2) ^a
$\text{Cr}(\text{OH})_2^{3+}$	575 (13.3)	405 (15.3)

^aReference 5.**Results and Discussion**

Addition of mercury(II) perchlorate to an acidic aqueous solution of $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$ results in rapid loss of the red-brown color of the organochromium species, as expected from eq 1. However, the visible spectrum of the solution immediately following reaction is not that of $\text{Cr}(\text{OH})_2^{3+}$. The absorption maxima are at wavelengths 3–4 nm smaller than those of $\text{Cr}(\text{OH})_2^{3+}$, and the intensities are about 30% higher. If the sample is left for several hours, its spectrum changes to that of $\text{Cr}(\text{OH})_2^{3+}$.

Cation-exchange chromatography at 4 °C of the solution immediately after reaction shows that two colored products are formed. The most easily eluted product is violet and has the ion-exchange properties and visible spectrum of $\text{Cr}(\text{OH})_2^{3+}$. The other product has a purple-red color and is more difficult to elute, indicating a charge $>+3$. This species was shown to contain chromium by formation of CrO_4^{2-} on reaction with alkaline hydrogen peroxide and mercury by deposition of $\text{Hg}(0)$ on copper wire. The characteristics of the visible spectrum are given in Table I.

Characterization of the higher charged product is subject to the usual problems with very soluble, paramagnetic species. However, it has been shown that it aquates quantitatively⁴ to $\text{Cr}(\text{OH})_2^{3+}$ with a rate constant of $1.27 \times 10^{-4} \text{ s}^{-1}$ (25 °C, 2.5 M HClO_4). This information, along with the composition data given above, and a comparison to the properties of $(\text{H}_2\text{O})_5\text{CrNCCH}_3^{3+}$,⁵ given in Table I, indicate that the species is

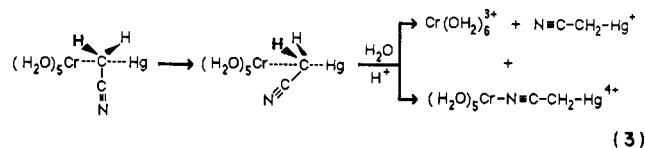


This formulation is consistent with the charge $>+3$, the presence of chromium and mercury, and the similarity in absorption maxima of I and $(\text{H}_2\text{O})_5\text{CrNCCH}_3^{3+}$. In addition, the unusual aquation lability of the latter ($k = 4 \times 10^{-4} \text{ s}^{-1}$, 25 °C)⁵ is consistent with that of this new species.

Quantitative product distribution studies were carried out by allowing $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$ ($5.0 \times 10^{-3} \text{ M}$) and $\text{Hg}(\text{ClO}_4)_2$ ($2.5 \times 10^{-3} \text{ M}$) to react in 0.05 M HClO_4 for 5 min and then separating

the products on Dowex 50W-X2 (H^+) at 4 °C. Of the total recovered chromium (92–93%), 48% was $\text{Cr}(\text{OH})_2^{3+}$ and 52% was I. Clearly, I is not a minor product of reaction 1.

The simplest mechanistic explanation for the formation of I seems to be that attack by Hg^{2+} induces inversion at the chromium-bonded carbon and this moves the nitrile function toward the chromium. Then the nitrile nitrogen can compete effectively with solvent water for the coordination site on chromium as the Cr–C bond is broken, as outlined in eq 3.



The process may be viewed as a mercury(II)-induced linkage isomerism on chromium(III). In that sense it has precedent in the studies of Orhanovic and Sutin⁶ on $(\text{H}_2\text{O})_5\text{Cr}-\text{SCN}^{2+} + \text{Hg}^{2+}$ and Espenson and Bushey⁷ on $(\text{H}_2\text{O})_5\text{Cr}-\text{CN}^{2+} + \text{Hg}^{2+}$. In both cases a dimetal product is formed. The thiocyanate system is most analogous to the present study in that 43% of the product is $(\text{H}_2\text{O})_5\text{Cr}-\text{NCS}-\text{Hg}^{4+}$ and 57% $\text{Cr}(\text{OH})_2^{3+}$, while with cyanide the only product is $(\text{H}_2\text{O})_5\text{Cr}-\text{NC}-\text{Hg}^{4+}$.

The reaction of $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CO}_2\text{H}$ with mercury(II) gives 100% $(\text{H}_2\text{O})_5\text{Cr}-\text{O}_2\text{CCH}_2-\text{Hg}^{4+}$.⁸ This observation was rationalized by assuming that the chromium(III) reactant actually was chelated. Now it appears possible that exclusive formation of the dimetal product might be due to more favorable competition by the $-\text{CO}_2\text{H}$ group compared to $-\text{CN}$ in a process analogous to eq 3.

Experimental Section

Materials. The solutions of $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$ were prepared from chromium(II) and ICH_2CN as described previously.³ The $\text{Hg}(\text{ClO}_4)_2$ solutions were made by dissolving a weighed amount of HgO (yellow) in aqueous perchloric acid. Analytical methods have been described previously.^{3,9}

Isolation of $[(\text{H}_2\text{O})_5\text{CrNCCH}_2\text{Hg}]^{4+}$. Typically, the required amount of a solution of $\text{Hg}(\text{ClO}_4)_2$ was added to a solution of known concentration of $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$ in 0.05 M $\text{HClO}_4/0.20 \text{ M LiClO}_4$. The reaction was allowed to proceed until the red color faded, and then the solution was diluted to an ionic strength $\leq 0.1 \text{ M}$ with ice-cold water and chromatographed at 4 °C on Dowex 50W-X2 in the H^+ form. $\text{Cr}(\text{OH})_2^{3+}$ was eluted with 0.5–1.0 M HClO_4 , and the binuclear product, with 2.5 M HClO_4 . The complex was stable for at least 24 h when stored at $<-5 \text{ }^\circ\text{C}$ in a freezer.

Instrumentation. The electronic spectra were recorded on a Cary 219 spectrophotometer. The hydrolysis of $(\text{H}_2\text{O})_5\text{CrNCCH}_2\text{Hg}^{4+}$ was monitored at 400 nm in a thermostated cell holder at 25 °C.

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(4) After hydrolysis, it is necessary to separate HgCH_2CN^+ from $\text{Cr}(\text{OH})_2^{3+}$ by ion-exchange chromatography in order to get the correct molar extinction coefficients for the chromium species because $\text{HgO}(\text{s})$ interferes with the chromate analysis.

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