$-H_{GF}$ and log $a^*_{H^+}$ vary over almost ten logarithmic units in the range of acid investigated.

It thus seems very hopeful that useful approximate values of hydronium ion activities in concentrated acid solutions can either be directly measured[4] or estimated.[1] The potential utility of such data in studying acid-catalyzed reactions is great, and is discussed in detail elsewhere.[9]

Acknowledgments. We are grateful to the National Research Council of Canada for financial support, and to Dr. J. Janata for helpful discussions.

(9) K. Yates and R. A. McClelland, *Progr. Phys. Org. Chem.*, in press.

Keith Yates,* R. A. McClelland
Department of Chemistry, University of Toronto
Toronto, Ontario M5S 1A1
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Anomalous Transition Metal Complex Promoted Rearrangement of Tricyclo[4.1.0.0^{2,7}]heptanes in Methanol[1]

Sir:

Our initial postulation[2] of the formation of a transition metal complexed carbene–transition metal bonded carbonium ion hybrid intermediate in the transition metal complex promoted rearrangement of derivatives of bicyclo[1.1.0]butanes[3] has now received substantial support.[4-8] Recently, Dauben and Kielbania confirmed our concept of an intermediate metal complexed carbene.[7] However, they questioned the validity of our suggestion[9] that a metal bonded cyclopropyl carbinyl cation might be a precursor of the observable metal complexed carbene. We now wish to report that transition metal complex promoted rearrangements of derivatives of bicyclo[1.1.0]butane in methanol are far more complex than either we or Dauben and Kielbania have indicated.

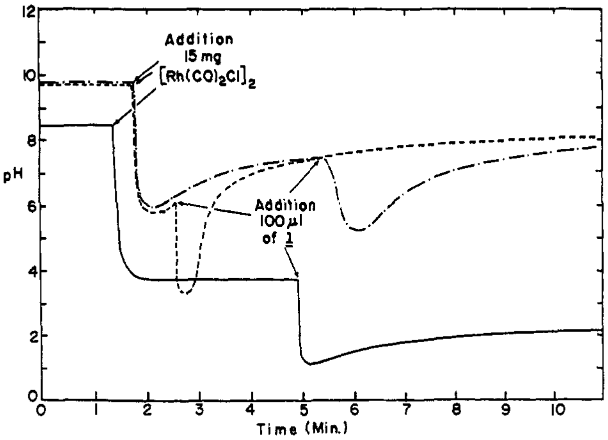
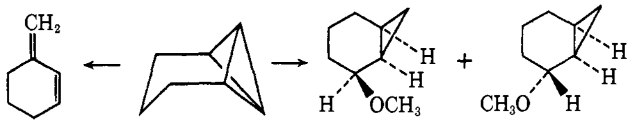


Figure 1. Plot of pH of a 3-ml sample of anhydrous methanol *vs.* time as a function of added sodium bicarbonate, added rhodium dicarbonyl chloride dimer, and added tricyclo[4.1.0.0^{2,7}]heptane. Solid line shows pH of methanol with no added sodium bicarbonate; dashed lines show plots of pH of methanol containing 10 mg of sodium bicarbonate per 3 ml of anhydrous methanol.



4 **1** **2** **3**

Whereas we had reported[9] that tricyclo[4.1.0.0^{2,7}]heptane[10] (**1**) gave a 75% yield of a mixture of **2** and **3** in methanol on addition of rhodium dicarbonyl chloride dimer, Dauben and Kielbania[7] showed that **1** gave 90% of **4**[11] and less than 10% of the mixture of **2** and **3** in methanol containing rhodium dicarbonyl chloride dimer and sodium bicarbonate. It was implied[7] that the apparent discrepancy between their finding and our results might be due to the use of aged rhodium dicarbonyl chloride dimer or to impure solvents. We have now found that the cause of this apparant discrepancy in results is associated with a much more fundamental aspect of the transition metal complex promoted rearrangement of bicyclo[1.1.0]butanes.[12] Our experiments indicated that the *product composition was determined by the rate of addition of the bicyclo-[1.1.0]butane derivative to the methanol solution of rhodium dicarbonyl chloride dimer and sodium bicarbonate* and not by the other factors suggested.[7] When **1** was added to a methanolic solution of rhodium dicarbonyl chloride dimer (both in the presence and absence of sodium bicarbonate) a rapid and dramatic drop occurred in the "pH" of the methanolic solution.[13] The extent of this pH drop was extremely short-lived in the presence of sodium bicarbonate; the amount of time required to return to the normal pH was a function of the amount of **1** added at any one instant. Figure 1 shows the plots of the pH of the methanolic solution under various conditions. As can be seen from this plot the addition of rhodium dicarbonyl chloride dimer (15 mg) to methanol (3 ml), both with and without added sodium bicarbonate (10 mg), provides a drop of 4–5 pH units. In the absence of sodium bicarbonate, this lowered pH remains reasonably constant.

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(1) Paper XXXIX of a series on The Chemistry of Bent Bonds. For the preceding paper see P. G. Gassman and R. R. Reitz, *J. Organometal. Chem.*, in press.

(2) P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **92**, 7631 (1970); P. G. Gassman, T. Atkins, and F. J. Williams, *ibid.*, **93**, 1812 (1971).

(3) For a more recent discussion see P. G. Gassman and F. J. Williams, *ibid.*, **94**, 7737 (1972), and following papers.

(4) R. Noyori, T. Suzuki, Y. Kumagai, and H. Takaya, *ibid.*, **93**, 5894 (1971).

(5) P. G. Gassman and T. Nakai, *ibid.*, **93**, 5897 (1971).

(6) Of particular significance are recent low-temperature nmr studies of intermediate species. Both Dauben's[7] and Masamune's[8] groups have interpreted their nmr spectral data in terms of a metal complexed carbene intermediate or its resonance form, the transition metal bonded carbonium ion.

(7) W. G. Dauben and A. J. Kielbania, Jr., *J. Amer. Chem. Soc.*, **94**, 3669 (1972).

(8) S. Masamune, M. Sakai, and N. Darby, *J. Chem. Soc., Chem. Commun.*, 471 (1972).

(9) P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **93**, 4597 (1971).

(10) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961).

(11) We had previously shown that **1** gave only **4** in nonprotic solvents.

(12) The results reported herein were reproducible with rhodium dicarbonyl chloride dimer which was (a) less than 2 hr old, (b) approximately 6 months old, and (c) a commercial sample (Strem Chemical) of unknown age and purity. Thus, the age of the complex is irrelevant. In all of our work solvent purity has been monitored with unusual care.

(13) The pH of the methanolic solution was monitored using a Metrohm-Herisau E-436 recording potentiometer with a Metrohm combination glass electrode EA-147. Ample precedent exists for the measurement of pH of methanolic solutions in this manner.[14]

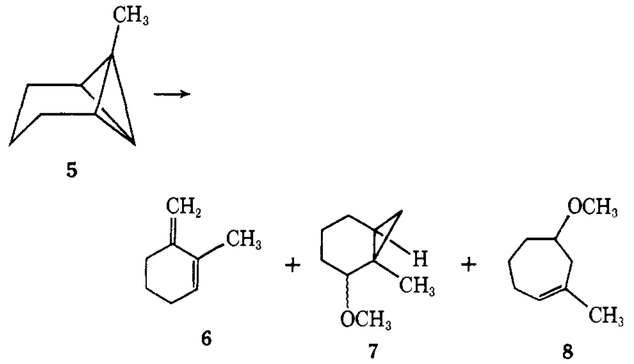
(14) For leading references and discussions of the measurement of pH in methanol see: R. G. Bates, "Determination of pH-Theory and Practices," Wiley, New York, N. Y., 1964, Chapter 8. See also C. D. Ritchie and P. D. Heffley, *J. Amer. Chem. Soc.*, **87**, 5402 (1965).

In the presence of sodium bicarbonate, the pH of the solution increases. During this period of pH increase the ability of the complex present in solution to promote the rearrangement of bicyclo[1.1.0]butanes decreases. This is presumably due to the destruction of the active complex by the methanolic sodium bicarbonate.

When 100 μl of **1** was injected into a vigorously stirred solution of 15 mg of rhodium dicarbonyl chloride dimer in 3 ml of dry methanol (containing *no* sodium bicarbonate) an immediate drop in pH from 3.7 to 1.1 was observed.[15] Under these conditions, **1** gave 6% of **4**, 15% of **2**, and 71% of **3**.[16]

When sodium bicarbonate was present, the magnitude of the pH drop was a function of time elapsed between the addition of the rhodium dicarbonyl chloride dimer and the addition of **1**. Rapid injection of 100 μl of **1** *ca.* 50 sec after the addition of the rhodium complex gave a pH drop of 2.8 units, while rapid injection after 3.5 min gave a 2.3-unit drop. This time pH dependence reflected the rate of disapperance of active rhodium complex in methanolic sodium bicarbonate. The rapid addition of **1** within 60 sec after the addition of the rhodium complex gave 15% of **4** and 75% of a 13:87 mixture of **2** and **3**. When 100 μl of **1** was added *dropwise* (neat) to the methanolic sodium bicarbonate solution immediately after the addition of the rhodium complex, only a small decrease in pH was noted for each drop. More importantly, the pH recovered to its original position between each drop. Under these conditions the pH of the solution remained above 5 throughout the period of time required for the isomerization of **1**. This method of dropwise addition resulted in the conversion of **1** into **4** (76% yield) and gave only trace amounts of **2** and **3**. These results clearly show that the formation of **2** and **3** results from an acid-catalyzed process which occurs below pH 5 in methanol, while the formation of **4** is presumably the result of the reaction of **1** with rhodium dicarbonyl chloride dimer or a related species. Thus, these results establish that the formation of **2** and **3** in methanol cannot be used as evidence for the intermediacy of a metal-bonded cyclopropylcarbinyl cation intermediate in the rhodium dicarbonyl chloride dimer promoted conversion of **1** into **4**.[17]

Similar results were obtained with 1-methyltricyclo$[4.1.0.0^{2,7}]$heptane (**5**). Rapid addition of **5** (neat) to a solution of rhodium dicarbonyl chloride dimer in methanol gave 3% of **6** and 95% of a mixture of the ethers represented by **7** and **8**. Again, pH monitoring showed a large pH drop on addition of **5**. Rapid addition of **5** (neat) to a methanolic solution containing both rhodium dicarbonyl chloride dimer and sodium bicarbonate gave a smaller pH drop, and yielded 22% of **6** and 64% of **7** and **8**. Dropwise addition of **5** (neat), under similar conditions, at a rate sufficient to maintain the pH above 5 gave 61% of **6** and only 3% of **7** and **8**. Thus, pH control, through regulated rate of addition of the bicyclo[1.1.0]butane derivative (**1** or **5**), can provide overwhelming control of the observed products.



Other transition metal complexes were checked to see if they had an acidifying effect in methanol. Rhodium norbornadiene chloride dimer did not produce an acidic solution in methanol, nor did the pH drop on addition of **1**. However, **1** was efficiently isomerized under these conditions to give **4** as the only product. Rhodium dicarbonyl acetylacetonate behaved in a manner similar to rhodium norbornadiene chloride dimer, except that the acetylacetonate complex promoted conversion of **1** to **4** was very slow and small amounts of **2** and **3** could be detected. Palladium chloride, π-allylpalladium chloride dimer, and bis(benzonitrilepalladium) chloride all gave pH profiles similar to rhodium dicarbonyl chloride dimer in methanol. In each case, addition of **1** caused a rapid, substantial decrease in the pH of the methanolic solution.

The major unanswered questions concern the nature of the acidic material which must account for the pH drop and the mechanism whereby **1** (or **5**) reacts with the transition metal complex in methanol to provide the rapid formation of this unidentified acid. The very transitory nature of these strongly acidic conditions indicates that the acidic material must react rapidly or undergo neutralization under the reaction conditions. It is not known at this time whether this acid is a mineral acid (hydrogen chloride) or a much more complex acid such as a metal hydride. We are continuing to investigate this problem.[18]

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Paul G. Gassman,* Robert R. Reitz
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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[15] A pH of 1.1 was also measured for a dry methanolic solution which was 5.6×10^{-4} *M* in hydrogen chloride.

[16] The ratio of **2**:**3** in the *absence* of added sodium bicarbonate was 17:83. The ratio of **2**:**3** obtained from **1** and dry methanolic hydrochloric acid was 15:85.

[17] It should be noted that these experiments merely rule out the use of certain results as evidence. They do not establish whether or not a metal-bonded cyclopropylcarbinyl cation is involved in the conversion of **1** into **4**.

[18] Subsequent to the completion of this study, it was reported that somewhat related behavior can be noted for silver ion [L. A. Paquette, S. E. Wilson, G. Zon, and J. A. Schwartz, *J. Amer. Chem. Soc.*, **94**, 9222 (1972)].

Studies in the Dihydropyridine Series. I. Novel and Stable Complexes of *N*-Methyl-3-ethyl-1,2-dihydropyridine and *N*-Methyl-3-ethyl-1,6-dihydropyridine

Sir:

Dihydropyridines have been involved as important intermediates in various biological systems. Thus, it is well established that the 1,4-dihydropyridine derivatives