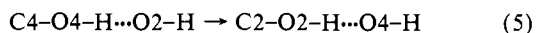


of the heptose the extended  $-\text{CHOHCH}_2\text{OH}$  side chain has a serious repulsive interaction with the hydroxyl at C-4. As a result this conformer is populated to a lesser extent and the proportion of the  $\alpha$ -pyranose in the equilibrium mixture is reduced.

The magnitudes of the deuterium isotope effects (see Table III) on the  $^{13}\text{C}$  chemical shifts of  $\beta$ -idopyranose differ only slightly from values observed for a series of other monosaccharides.<sup>8</sup> For  $\alpha$ -idopyranose, however, both the magnitudes and the multiplicities are substantially different. Thus,  $\Delta_\beta$  for carbon 1 (61 ppb) is much smaller than normally observed ( $106 \pm 9$  ppb).<sup>8</sup> Also, carbons 2, 3, and 4 experience long-range isotope effects, beyond the ones expected from the directly bonded hydroxyls and the hydroxyls on vicinal carbons. Similar phenomena observed for  $\alpha$ -talopyranose<sup>8</sup> and some  $\beta$ -diols<sup>1</sup> have been interpreted in terms of isotopic perturbations of equilibria involving intramolecular hydrogen bonds. In the  ${}^4\text{C}_1$  conformation of  $\alpha$ -D-idopyranose the two pairs of syn-diaxial hydroxyls on carbons 1 and 3 and carbons 2 and 4 are ideally situated for intramolecular hydrogen bonding. Indeed the involvement of these hydroxyls in such bonds has been inferred from proton NMR data on idose derivatives.<sup>22,23</sup> One of the equilibria is



Deuteration of either O4-H or O2-H is likely to perturb this equilibrium with the results sensed by carbons 2 and 4, respectively. The situation is similar to the one described in detail for  $\alpha$ -talopyranose.<sup>8</sup> Hydroxyls attached to anomeric carbons seem to participate in hydrogen bonds almost exclusively as the hydrogen donors.<sup>24</sup> Therefore, for the hydroxyls on carbons 1 and 3 an equilibrium involving structures with and without the C1-O1-H $\cdots$ O3-H hydrogen bond is suggested. Isotopic perturbation of this equilibrium upon deuteration of the anomeric hydroxyl results in the additional isotope effect on the chemical shift of carbon 3 and in modification of the intrinsic isotope effect on the chemical shift of carbon 1. The chemical shift manifestation of isotopic

perturbation on an equilibrium is more probable when the equilibrium constant is close to unity.<sup>8</sup> The absence of extra splittings in the isotopic multiplets of  $\beta$ -idopyranose, where an equilibrium involving the hydroxyls on carbons 2 and 4 (eq 5) is also possible, indicates that one of the structures in the equilibrium is strongly favored.

For  $\alpha$ -D-idopyranose, the preponderance of intramolecular hydrogen bonding interactions in the nonaqueous solvent<sup>17</sup> is probably one of the main factors responsible for the shift toward the  ${}^4\text{C}_1$  conformation, in which such interactions are possible. Moreover, the accessibility of several states with intramolecular hydrogen bonds (as the isotopic multiplets have demonstrated) leads to further stabilization of this conformation. However, these relatively weak interactions should have little direct effect on the tautomeric equilibrium, which proceeds on an energy scale corresponding to the breaking and formation of covalent bonds. Entropic considerations suggest that the conformational equilibrium is affected by the number of states available to each conformer, whereas the tautomeric equilibrium is affected by the number of conformers for each species.

### Conclusions

The solvent dependence of the tautomeric composition and  $^{13}\text{C}$  chemical shifts of D-idose as well as the deuterium isotope effects and the isotopic multiplets all lead to the following simple picture. In going from an aqueous to a nonaqueous solvent,  $\alpha$ -D-idopyranose, originally present as a mixture of conformers, assumes almost exclusively the  ${}^4\text{C}_1$  conformation, which is stabilized by intramolecular hydrogen bonding interactions. The conformational equilibrium of the  $\alpha$ -pyranose form appears to be the key phenomenon in solutions of D-idose.

**Acknowledgment.** The excellent technical assistance of David S. Rice is greatly appreciated. I thank Professor S. J. Angyal for helpful correspondence, Drs. J. C. Gast and R. G. Nickol for their comments on the manuscript, and Mark A. Bennett for his assistance with the computer simulations.

**Registry No.**  $\alpha$ -P, 7282-82-8;  $\beta$ -p, 7283-02-5;  $\alpha$ -f, 41847-67-0;  $\beta$ -f, 40461-75-4; D<sub>2</sub>, 7782-39-0; D-idose, 5978-95-0.

(22) Paulsen, H.; Friedmann, M. *Chem. Ber.* **1972**, *105*, 705-717.

(23) Angyal, S. J.; Kondo, Y. *Carbohydr. Res.* **1980**, *81*, 35-48.

(24) Jeffrey, G. A.; Takagi, S. *Acc. Chem. Res.* **1978**, *11*, 264-270.

## Transition-Metal-Carbene Chemistry. Structure, Thermodynamics, and Reactivity of $\text{RhCH}_2^+$ in the Gas Phase

D. B. Jacobson<sup>†</sup> and B. S. Freiser\*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received July 3, 1984

**Abstract:** The first studies involving a second-row transition-metal methyldene ion,  $\text{RhCH}_2^+$ , in the gas phase using Fourier transform mass spectrometry (FTMS) are described. Product distributions for the reactions of  $\text{RhCH}_2^+$  with hydrogen, methane, ethane, ethene, propene, and cyclopropane are reported. The methylene bond strength,  $D^\circ(\text{Rh}^+-\text{CH}_2)$ , was bracketed between 92 and 95 kcal/mol from which  $D^\circ(\text{Rh}^+-\text{CH}_2) = 94 \pm 5$  kcal/mol is assigned. Structural studies clearly indicate formation of a methyldene-rhodium complex instead of a hydrido-methyldyne species. Collisional activation of  $\text{RhCH}_2^+$  yields both  $\text{RhC}^+$  and  $\text{Rh}^+$ , suggesting that  $\alpha$ -hydride abstraction in  $\text{RhCH}_2^+$  can occur.  $\text{RhCH}_2^+$  reacts readily with both hydrogen and methane and represents the first example of methane activation by a cationic mononuclear transition-metal complex in the gas phase. The activation energy for methane elimination from  $\text{Rh}(\text{H})(\text{CH}_3)^+$  appears to be less than 5 kcal/mol.  $\alpha$ -Hydride abstraction from  $\text{Rh}(\text{CH}_3)_2^+$  resulting in methane elimination is found to be facile. Reactions of  $\text{Rh}^+$  with cyclopropane and  $\text{RhCH}_2^+$  with ethene suggest that  $\beta$ -hydride elimination from a rhodacyclobutane intermediate occurs readily. Therefore, the rhodacyclobutane<sup>+</sup> ring is believed to have significant puckering. Finally, metathesis products are observed for reactions of  $\text{RhCD}_2^+$  with both ethene and propene. The results of this work are compared to earlier studies on first-row  $\text{MCH}_2^+$  ions.

Transition metal-carbenes<sup>1,2</sup> have been implicated as intermediates in a variety of important catalytic transformations including olefin metathesis,<sup>3-7</sup> the Ziegler-Natta polymerization of olefins,<sup>8,9</sup> cyclopropane formation from olefins,<sup>10,11</sup> olefin ho-

mologation,<sup>12</sup> metal-alkyl decompositions,<sup>13-15</sup> and the heterogeneous Fischer-Tropsch process.<sup>16</sup> Despite the important role

<sup>†</sup> Current address: Department of Chemistry, California Institute of Technology, Pasadena, California 91125.

(1) Dotz, K. H.; Fischer, H.; Hofmann, P.; Kreisler, F. R.; Schubert, U.; Weiss, K. "Transition Metal Carbene Complexes"; Verlag Chemie: Weinheim, 1983; also references therein.

**Table I.** Summary of Metal-Carbene Bond Dissociation Energies for the First-Row Transition-Metal Ions<sup>a</sup>

$D^0(M^+-CH_2)$					
V <sup>+</sup>	Cr <sup>+</sup>	Mn <sup>+</sup>	Fe <sup>+</sup>	Co <sup>+</sup>	Ni <sup>+</sup>
80 ± 5 <sup>b</sup>	65 ± 7 <sup>c</sup>	94 ± 7 <sup>c</sup>	96 ± 5 <sup>c</sup>	85 ± 7 <sup>d</sup>	86 ± 6 <sup>c</sup>

<sup>a</sup>All values in kcal/mol. <sup>b</sup>Reference 24. <sup>c</sup>Reference 23. <sup>d</sup>Reference 22.

that metal-carbenes apparently play in catalytic transformations, few unsubstituted transition-metal-carbene complexes (methylidenes) have been prepared and studied.<sup>17</sup> In addition little is known about the thermochemistry of these species. Relative strengths of  $\pi$  bonds in these species are sometimes derived from measured rotational barriers.<sup>18</sup> This analysis, however, may lead to erroneous conclusions for metal systems in which more than a single d orbital is available for  $\pi$  bonding.<sup>19</sup> Theoretical calculations for model metal-carbene systems yield estimates of the bond strengths.<sup>20,21</sup> Beauchamp and co-workers and more recently

Armentrout and co-workers, using ion beam techniques, have determined  $D^0(M^+-CH_2)$  directly for the first-row atomic transition-metal ions V-Ni (Table I).<sup>22-24</sup> Beauchamp and co-workers have also investigated fluorine substituent effects on nickel-(+)-carbene bond dissociation energies and found  $D^0(Ni^+-CF_2) = 47 \pm 7$  kcal/mol.<sup>25</sup> The experimental values compare poorly with the theoretical numbers, suggesting that caution must be employed regarding these bond strengths.

The gas-phase chemistry of  $MnCH_2^+$ ,<sup>26</sup>  $FeCH_2^+$ ,<sup>27</sup> and  $CoCH_2^+$ <sup>27</sup> has been studied. Briefly, these carbenes yield metathesis products with olefins. The reactions of both  $CoCH_2^+$  and  $FeCH_2^+$  with aliphatic and cyclic alkanes were also studied. These carbenes react with aliphatic alkanes predominantly by attacking C-H bonds. This is in contrast to the corresponding atomic species which predominantly attack C-C bonds of aliphatic alkanes.<sup>28,29</sup> These results suggest that a carbene ligand can dramatically affect the chemistry of atomic transition-metal ions in the gas phase.

Here we present the first studies involving a second-row transition-metal-carbene ion,  $RhCH_2^+$ , in the gas phase using Fourier transform mass spectrometry. The structure, thermochemistry, and reactivity of this ion are probed and discussed in light of previous studies on the reactions of  $Rh^+$  with alkanes.<sup>30</sup>

## Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectrometry<sup>31</sup> and Fourier transform mass spectrometry (FTMS)<sup>32</sup> have been discussed elsewhere. All experiments were performed by using a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail<sup>33</sup> and equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell was constructed in our laboratory and includes a  $1/4$ -in.-diameter hole in one of the transmitter plates which permits irradiation with various light sources. A high-purity rhodium foil is supported on the opposite transmitter plate. Metal ions are generated by focussing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) onto the rhodium foil.<sup>34</sup>

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze-pump-thaw cycles to remove non-condensable gases. Ethylene- $d_4$  oxide was obtained from MSD Isotopes (Merck Chemical Division) containing >98 atom % deuterium. Sample pressures were on the order of  $1 \times 10^{-7}$  torr. Argon was used as the collision gas for the collision-induced dissociation (CID)<sup>35</sup> experiments at a total sample pressure of approximately  $5 \times 10^{-6}$  torr. A Bayard-

(2) (a) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. (b) Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487. (c) Cardin, D. J.; Cetinkaya, B.; Doyle, M. J.; Lappert, M. F. *Chem. Rev.* **1973**, *73*, 545. (d) Cardin, D. J.; Cetinkaya, B.; Doyle, M. J.; Lappert, M. F. *Chem. Soc. Rev.* **1973**, *2*, 99. (e) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.

(3) Herisson, J. L.; Chauvin, T. *Makromol. Chem.* **1970**, *141*, 161.

(4) (a) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. (b) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449. (c) Katz, T. J. *Adv. Organomet. Chem.* **1977**, *16*, 283. (d) Casey, C. P.; Scheck, D. M.; Shusterman, A. J. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3, p 141.

(5) (a) Grubbs, R. H.; Hopper, C. J. *J. Am. Chem. Soc.* **1979**, *101*, 1499. (b) Grubbs, R. H.; Miyashita, A. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3, p 151. (c) Mocella, M. T.; Rovner, R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 4689. (d) Grubbs, R. H. *Inorg. Chem.* **1979**, *18*, 2623.

(6) (a) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 7808. (b) Casey, C. P.; Tuinstra, H. E.; Saemen, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 608.

(7) (a) Grubbs, R. H.; Buck, P. L.; Can, D. D. *J. Am. Chem. Soc.* **1975**, *97*, 3265. (b) Grubbs, R. H.; Cay, D. D.; Hoppin, C.; Burk, P. L. *J. Am. Chem. Soc.* **1976**, *98*, 3478. (c) Katz, T. J.; McGinnis, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 1592. (d) Katz, T. J.; Rothchild, R. *J. Am. Chem. Soc.* **1976**, *98*, 2519.

(8) (a) Irvin, K. J.; Rooney, J. J.; Stewart, C. C.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604. (b) Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27.

(9) (a) Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331. (b) Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942.

(10) (a) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. (b) Reference 6a.

(11) (a) Casey, C. P.; Shusterman, A. J. *J. Mol. Catal.* **1980**, *8*, 1. (b) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754.

(12) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(13) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219.

(14) (a) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 209. (b) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 761. (c) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121.

(15) (a) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210. (b) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774. (c) Fellman, J. D.; Schrock, R. R.; Traficante, D. D. *Organometallics* **1982**, *1*, 481. (d) Edwards, D. S.; Biondy, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505.

(16) (a) Herrman, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (b) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (c) Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447. (d) Biloen, P.; Sachtler, W. M. H. *Adv. Catal.* **1981**, *30*, 165. (e) Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181. (f) Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1981**, *103*, 1287.

(17) (a) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577. (b) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

(18) (a) Kiel, W. A.; Lin, G. Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (b) Kegley, S. E.; Brookhart, M. *Organometallics* **1982**, *1*, 760.

(19) Francl, M. M.; Pietro, W. J.; Hout, R. F., Jr.; Hehre, W. J. *Organometallics* **1982**, *2*, 281.

(20) (a) Rappe, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1977**, *99*, 3966. (b) Carter, E. A.; Goddard, W. A., III. *J. Phys. Chem.* **1984**, *88*, 1485. (c) Carter, E. A.; Goddard, W. A., III. *Organometallics*, submitted.

(21) (a) Brooks, B. R.; Schaefer, H. F., III. *Mol. Phys.* **1977**, *34*, 193. (b) Vincent, M. A.; Yoshioka, Y.; Schaefer, H. F., III. *J. Phys. Chem.* **1982**, *86*, 3905.

(22) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819.

(23) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501.

(24) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 4065.

(25) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1829.

(26) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 6449.

(27) (a) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 2605.

(b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 67. (c) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 4373.

(28) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (b) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (c) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818.

(29) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197.

(30) Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 5944.

(31) For reviews on ICR see: (a) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527. (b) Lehman, T. A.; Bursey, M. M. "Ion Cyclotron Resonance Spectrometry"; Wiley-Interscience: New York, 1976. (c) Wanczek, K. P. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *60*, 11.

(32) (a) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *26*, 489. (b) Marshall, A. G.; Comisarow, M. B. *J. Chem. Phys.* **1979**, *71*, 4434. (c) Gaderi, S.; Kulkarni, P. S.; Ledford, E. B.; Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 428.

(33) (a) Cody, R. B.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *41*, 199. (b) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96.

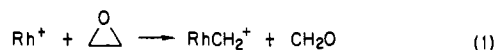
(34) For details of the laser ionization technique see: (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641. (b) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360.

(35) Cooks, R. G. "Collision Spectroscopy"; Plenum Press: New York, 1978.

Alpert ionization gauge was used to monitor pressure.

Details of CID in conjunction with FTMS have been described elsewhere.<sup>33,36-38</sup> The collision energy of the ions can be varied (typically between 0 and 100 eV) from which plots of CID product ion intensities vs. ion kinetic energy can be made. These plots are reproducible to  $\pm 5\%$  absolute and yield additional structural information. The spread in ion kinetic energy is dependent on the total average kinetic energy and is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.<sup>39</sup>

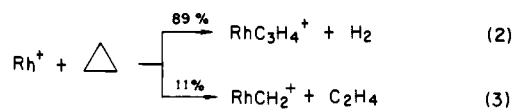
The  $\text{RhCH}_2^+$  ions were formed by reaction of laser-generated  $\text{Rh}^+$  with ethylene oxide, reaction 1. Labeled carbene ( $\text{RhCD}_2^+$ ) was formed



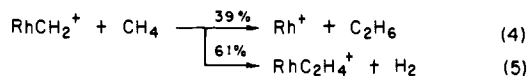
by reaction with deuterated ethylene oxide. The ethylene oxide reagent gas was introduced into the vacuum chamber through a General Valve Corp. Series 9 pulsed solenoid valve.<sup>40</sup> Both the laser and the valve are pulsed concurrently. The pulsed reagent gas fills the vacuum chamber to a maximum pressure of  $\sim 10^{-5}$  torr and is pumped away by a high-speed 5-in. diffusion pump in  $\sim 250$  ms. The  $\text{RhCH}_2^+$  ( $\text{RhCD}_2^+$ ) ions are then isolated by swept double resonance ejection techniques<sup>32,41</sup> and allowed to react with a static pressure of a specific reagent gas without complicating reactions with ethylene oxide.<sup>42</sup>

## Results and Discussion

**Bond Energy of  $\text{Rh}^+-\text{CH}_2$ .**  $\text{Rh}^+$  reacts with cyclopropane to yield both dehydrogenation and ethene elimination,<sup>43</sup> reactions 2 and 3. Reaction 3 implies  $D^\circ(\text{Rh}^+-\text{CH}_2) > 92.2 \pm 1$  kcal/mol.<sup>44</sup>



Methane reacts readily with  $\text{RhCH}_2^+$ , generated in reactions 1 or 3, producing  $\text{Rh}^+$  and  $\text{RhC}_2\text{H}_4^+$ , reactions 4 and 5. Observation



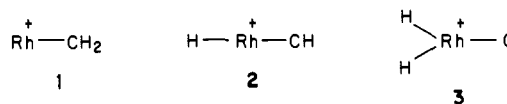
of reaction 4 places an upper limit of  $94.7 \pm 1$  kcal/mol for  $D^\circ(\text{Rh}^+-\text{CH}_2)$ .<sup>44</sup> Reactions 3 and 4, therefore, provide an absolute bracketing of  $D^\circ(\text{Rh}^+-\text{CH}_2)$  between  $92.2 \pm 1$  and  $94.7 \pm 1$  kcal/mol from which  $D^\circ(\text{Rh}^+-\text{CH}_2) = 94 \pm 5$  kcal/mol is assigned. This value is comparable to those for the first-row transition-metal-carbene ions (Table I).

The  $\text{Rh}^+-\text{CH}_2$  bond strength can be compared to  $D^\circ(\text{Rh}^+-\text{CH}_3) = 47 \pm 5$  kcal/mol.<sup>45</sup> The  $\text{Rh}^+-\text{CH}_3$  bonding was modeled

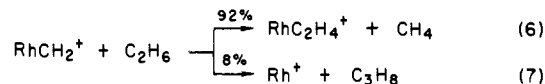
semiquantitatively by using simple covalent and electrostatic bonding models<sup>45</sup> and was found to be predominantly covalent in character with the metal contribution to the bond being mostly d like.<sup>45</sup> This is in contrast to the first-row transition-metal-methyls ( $\text{M}^+-\text{CH}_3$ ) where correlation of experimental  $\text{M}^+-\text{CH}_3$  bond strength with electronic promotion energies ( $3d \rightarrow 4s$ ) of the metal ions indicates that the metal orbital involved in bonding consists primarily of 4s character.<sup>23</sup>

The bonding in  $\text{Rh}^+-\text{CH}_2$  probably involves predominantly metal orbitals of d character; however, a full understanding of the bonding in  $\text{Rh}^+-\text{CH}_2$  must await detailed theoretical calculations.

**Structure of  $\text{RhCH}_2^+$ .** The  $\text{RhCH}_2^+$  ions may consist of three basic structures, 1-3. Reactions of metal complexes in the gas phase with both deuterium<sup>30,46-48</sup> and ethylene- $d_4$ <sup>49</sup> have been used

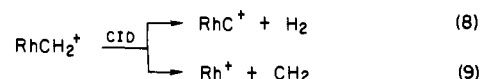


to probe metal-hydride character. If  $\text{RhCH}_2^+$  consisted of either structures 2 or 3, then H/D exchange with deuterium and ethylene- $d_4$  would be predicted; however, none was observed. This provides evidence against the hydride structures, 2 and 3. Ethane reacts rapidly with  $\text{RhCH}_2^+$  to yield  $\text{RhC}_2\text{H}_4^+$  and  $\text{Rh}^+$ , reactions 6 and 7.  $\text{RhCD}_2^+$  yields complete loss of label upon reaction with



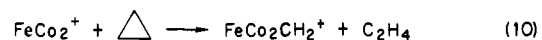
ethane. These results indicate that  $\text{RhCH}_2^+$  is composed formally of methylidene bound to  $\text{Rh}^+$ , 1, instead of the hydrido species 2 and 3.

Collisional activation of  $\text{RhCH}_2^+$  results in both dehydrogenation and  $\text{CH}_2$  elimination, reactions 8 and 9. Process 9 accounts



for over 90% of the fragmentation at all of the kinetic energies studied (0-100 eV). The small amount of dehydrogenation, process 8, provides further evidence against structure 3 since it should yield facile reductive elimination of hydrogen. Both  $\text{FeCH}_2^+$  and  $\text{CoCH}_2^+$  yield exclusively  $\text{CH}_2$  elimination upon collisional activation.

Process 8 may proceed by an initial  $\alpha$ -hydride abstraction forming 2 followed by a second abstraction forming 3.  $\alpha$ -Hydride abstractions have been observed for alkylidene complexes in solution<sup>50</sup> as well as an equilibrium between  $d^2$  alkylidene and  $d^\circ$  alkylidyne complexes.<sup>51,52</sup> CID of  $\text{FeCo}_2\text{CH}_2^+$ , generated in reaction 10, yields exclusively dehydrogenation to form  $\text{FeCo}_2\text{C}^+$  in high efficiency.<sup>53</sup> Structural studies suggest formation of a



methylidene-cluster complex in reaction 10. Dehydrogenation of the above cluster may be facilitated by formation of three-centered two-electron C-H-M bonds. For example, such a deformation has been documented for unsaturated methylidyne clusters.<sup>54</sup> Such a bonding scheme, however, is not possible for

(36) McIver, R. T., Jr.; Bowers, W. D. "Tandem Mass Spectrometry"; McLafferty, F. W., Ed.; John Wiley and Sons: New York, 1983; p 287.

(37) Burnler, R. C.; Cody, R. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 7436.

(38) (a) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736.

(b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484.

(39) Huntress, W. T.; Mosesman, M. M.; Elleman, D. D. *J. Chem. Phys.* **1971**, *54*, 843.

(40) A detailed description of pulsed valve introduction of reagent gases in conjunction with FTMS can be found in the following: Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.

(41) Byrd, G. D. Ph.D. Thesis, Purdue University, West Lafayette, IN, 1982.

(42) This methodology is described in more detail in the following: Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3891.

(43) In addition to these products an earlier study of ours<sup>30</sup> indicated formation of small amounts (<7% total) of  $\text{RhC}_2\text{H}_4^+$  and  $\text{RhC}_2\text{H}_3^+$ . A careful examination revealed that these products are probably the result of reaction with translationally excited  $\text{Rh}^+$ .

(44) Calculated with the heats of formation from the following: Rosenstock, H. M.; Draxl, D.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem., Ref. Data Suppl.* **1977**, *6*.  $\Delta H_f^\circ(\text{CH}_2) = 92.4$  kcal/mol; Chase, M. W.; Curnett, J. L.; Prophet, H.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem., Ref. Data Suppl.* **1975**, *4*. Heats of formation of radicals taken from the following: McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. It is assumed that the  $\text{RhCH}_2^+$  generated does not contain excessive internal energy and that an appreciable reaction rate implies an exothermic process.

(45) Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4403.

(46) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492.

(47) Carlin, T. J.; Sallans, L.; Cassidy, C. J.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 6320.

(48) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967.

(49) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.

(50) Fellmann, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6608.

(51) Churchill, M. R.; Wasserman, H. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1710.

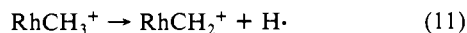
(52) (a) Holmes, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 4599.

(b) Holmes, S. J.; Clark, D. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6332.

(53) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 5352.

a mononuclear methylidyne complex. The dehydrogenation reaction 8 may also proceed by direct elimination of hydrogen by the methylidene group. Finally, formation of  $\text{RhC}^+$  by reaction 8 may be facilitated by the strong  $\text{Rh}^+-\text{C}$  bond,  $>145$  kcal/mol.<sup>55</sup>

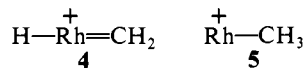
The above  $\text{Rh}^+-\text{CH}_2$  bond energy together with the recently determined  $\text{Rh}^+-\text{CH}_3$  and  $\text{Rh}^+-\text{H}$  bond strengths<sup>45</sup> may be used to infer the structure of  $\text{RhCH}_3^+$ . The overall endothermicity for process 11 is calculated to be  $62 \pm 10$  kcal/mol.<sup>56</sup> This value



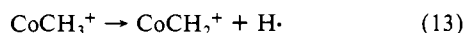
is nearly half that for process 12, 109 kcal/mol, but is close to



that for  $D^\circ(\text{Rh}^+-\text{H}) = 42 \pm 3$  kcal/mol.<sup>45</sup> The structure of  $\text{RhCH}_3^+$  is, therefore, believed to consist of a hydrido-methylidene complex, **4**, rather than the methyl species, **5**. For comparison, the endothermicity for the cobalt congener, process 13, is  $85 \pm$

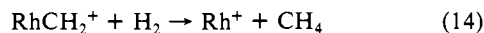


8 kcal/mol.<sup>28a</sup> Beauchamp and co-workers, using this value, suggested that  $\text{CoCH}_3^+$  consists formally of a metal-methyl



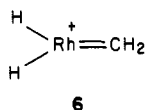
structure since the above bond energy is more representative of a C-H bond weakened by resonance stabilization of the  $\text{CoCH}_2^+$  product, rather than a  $\text{Co}^+-\text{H}$  bond ( $52 \pm 4$  kcal/mol).<sup>28a</sup> We corroborated Beauchamp's assertion of the  $\text{CoCH}_3^+$  structure by experiments which clearly ruled out a hydride-methylidene structure.<sup>42,57</sup>

**Reactions with  $\text{H}_2$ .**  $\text{RhCH}_2^+$  reacts rapidly with hydrogen, resulting in elimination of methane, reaction 14. This process requires  $D^\circ(\text{Rh}^+-\text{CH}_2)$  be less than 110 kcal/mol<sup>44</sup> in accordance with our assigned value. Deuterium reacts analogously to hydrogen with no H/D scrambling observed. This is only the second



reported example, of which we are aware, of oxidative addition of hydrogen to a metal complex in the gas phase.<sup>58</sup> A  $\text{CpRhC}_3\text{H}_5^+$  complex has been reported to undergo 4 H/D exchanges with deuterium in the gas phase.<sup>48</sup> In this case deuterium was proposed to initially oxidatively add to the complex followed by reversible transfer to the allyl ligand followed by reductive elimination of HD. The oxidative addition of molecular hydrogen and the corresponding reverse reductive elimination are important elementary processes in many catalytic and synthetic reactions.<sup>59</sup>

Reaction 14 may proceed by initial oxidative addition of hydrogen to  $\text{RhCH}_2^+$  to generate **6**, followed by successive hydride



shifts to the ligand resulting in reductive elimination of methane. The reverse process has been proposed for the dehydrogenation of methane by kinetically excited  $\text{Fe}^+$ ,  $\text{Co}^+$ , and  $\text{Ni}^+$  in an ion beam instrument.<sup>28</sup> Alternatively, addition of hydrogen may

(54) (a) Beno, M. A.; Williams, J. M.; Tackikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 1485. (b) Gavin, R. M.; Reutt, J.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 3981.

(55) Jacobson, D. B.; Byrd, G. D.; Freiser, B. S. *Inorg. Chem.* **1984**, *23*, 553.

(56) This calculation is based on  $D^\circ(\text{Rh}^+-\text{CH}_3) = 47 \pm 5$  kcal/mol and  $D^\circ(\text{Rh}^+-\text{CH}_2) = 94 \pm 5$  kcal/mol. No a priori assumption on the  $\text{RhCH}_3^+$  structure is required.

(57) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.

(58) A  $\text{RhC}_7\text{H}_6^+$  complex readily adds hydrogen generating  $\text{RhC}_7\text{H}_8^+$ . Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 1159.

(59) (a) Collman, J. P. *Acc. Chem. Res.* **1968**, *1*, 136. (b) Vaska, L.; Werneke, M. F. *Trans. N.Y. Acad. Sci.* **1971**, *33*, 70. (c) Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386. (d) Longato, B.; Morandini, F.; Bresadola, S. *Inorg. Chem.* **1976**, *15*, 650.

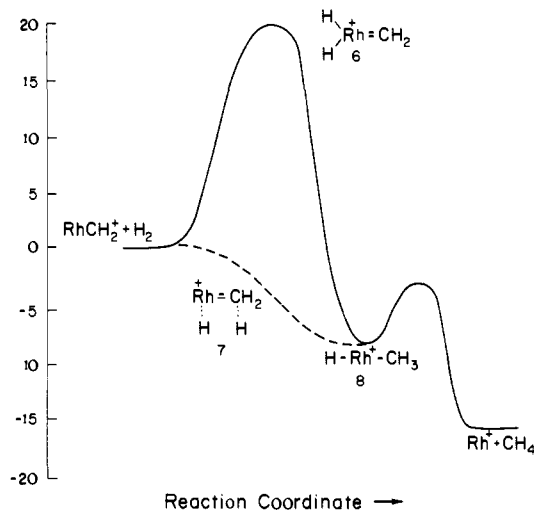
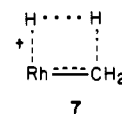


Figure 1. Reaction coordinate diagram illustrating the energetics of the reaction between  $\text{RhCH}_2^+$  and  $\text{H}_2$ . The vertical axis is in kcal/mol.

proceed through a four-centered intermediate, **7**. A potential energy diagram for the elimination of methane from  $\text{RhCH}_2^+$  and



hydrogen, reaction 14, is shown in Figure 1. In this diagram  $D^\circ(\text{Rh}^+-\text{CH}_2) = 94$  kcal/mol was used, vide infra. Using  $D^\circ(\text{Rh}^+-\text{H}) = 42 \pm 5$  kcal/mol<sup>45</sup> yields formation of **6** as roughly  $20 \pm 10$  kcal/mol endothermic. It appears, therefore, to be an unlikely intermediate. Alternatively, addition of hydrogen may proceed through a four-centered intermediate, **7**, which ultimately rearranges to **8**, a hydrido-methyl complex. Steingerwald and Goddard,<sup>60</sup> using generalized valence bond methods, have studied the H/D exchange reaction of  $\text{Cl}_2\text{MH}$  ( $\text{M} = \text{Sc}, \text{Ti}, \text{Ti}^+$ ) with  $\text{D}_2$  proceeding through a four-centered transition state. In addition, Watson has recently observed an interesting methane exchange reaction which may well proceed through a four-centered transition state.<sup>61</sup> Using  $D^\circ(\text{Rh}^+-\text{H}) = 42 \pm 5$  kcal/mol and  $D^\circ(\text{Rh}^+-\text{CH}_3) = 47 \pm 5$  kcal/mol<sup>45</sup> yields formation of **8** as being essentially thermoneutral. Given the above uncertainties, formation of **8** is believed to be roughly 5–10 kcal/mol exothermic. Absence of H/D exchange of  $\text{RhCH}_2^+$  with deuterium indicates that dehydrogenation of **8** is much slower than reductive elimination of methane and, therefore, that the activation barrier for reductive elimination of methane is quite low and certainly less than the barrier for dehydrogenation and is thus assigned as 5 kcal/mol. The activation energies for reductive elimination of methane from platinum complexes were found to be low.<sup>62</sup> Theoretical calculations on the reductive elimination of methane from  $\text{Pt}^{\text{II}}(\text{H})(\text{CH}_3)(\text{PH}_3)_2$  gave an activation energy of 28 kcal/mol.<sup>63</sup> The activation energy for reductive elimination of ethane from  $(\text{CO})\text{Co}(\text{CH}_3)_2^+$  is believed to exceed 20 kcal/mol.<sup>64</sup>

Both  $\text{FeCH}_2^+$  and  $\text{CoCH}_2^+$  are essentially unreactive with hydrogen and deuterium even though formation of methane in analogy to reaction 14 is exothermic by  $14 \pm 5$  and  $25 \pm 7$  kcal/mol, respectively.<sup>64</sup> This may be due to a barrier for initial addition of hydrogen to the complex preventing formation of intermediates **6–8**. Alternatively, the barrier for reductive elim-

(60) Steingerwald, M. L.; Goddard, W. A., III *J. Am. Chem. Soc.* **1984**, *106*, 308.

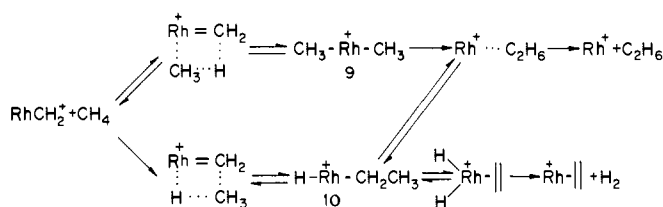
(61) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491.

(62) (a) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457. Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.

(63) Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 7482.

(64) These calculations are based on  $D^\circ(\text{Fe}^+-\text{CH}_3) = 96 \pm 5$  kcal/mol from ref 23 and  $D^\circ(\text{Co}^+-\text{CH}_2) = 85 \pm 7$  kcal/mol from ref 22.

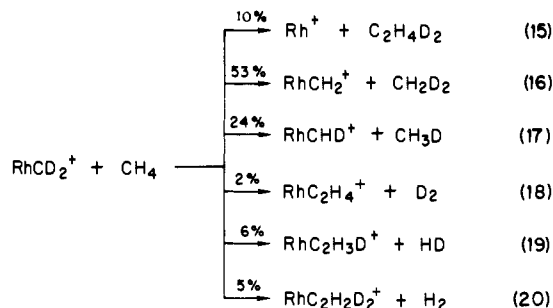
Scheme I



ination of methane from intermediate **8** may be large. Since no H/D exchange is observed for these carbenes, however, it appears that a hydrido-methyl complex is never formed. Therefore, the inert behavior of these carbenes with hydrogen is *not* due to a large barrier for reductive elimination of methane from **8** but due to the barrier for initial addition of hydrogen.

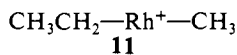
**Reactions with Methane and Ethane.** Methane reacts slowly ( $k \sim 1 \times 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) with  $\text{RhCH}_2^+$  by reactions 4 and 5 as stated above and is the first example of methane activation by a cationic mononuclear transition-metal complex in the gas phase.<sup>65,66</sup> Structural studies on  $\text{RhC}_2\text{H}_4^+$  formed in reaction 5 are consistent with a  $\text{Rh}(\text{ethene})^+$  complex. A mechanism for this reaction is shown in Scheme I and, by the analogous arguments used for  $\text{H}_2$ , involves four-centered intermediates, forming either  $(\text{CH}_3)_2\text{Rh}^+$ , **9**, or the hydrido-ethyl complex, **10**. Since reaction 4 is essentially thermoneutral and there are usually substantial barriers for reductive elimination of ethane from dimethyl complexes,<sup>62,67-69</sup> it seems unlikely that intermediate **9** leads to  $\text{Rh}^+$  formation.

$\text{RhCD}_2^+$  reacts more readily with methane than  $\text{RhCH}_2^+$  to yield a variety of products, reactions 15–20. The thermoneutral methylidene exchange reactions 16 and 17 dominate and account



for the increase in reactivity of  $\text{RhCD}_2^+$  over  $\text{RhCH}_2^+$  with methane. The methylidene exchange reactions probably proceed by an "equilibrium" between the  $(\text{CH}_3)_2\text{Rh}^+$  complex, **9**, and its corresponding four-centered intermediate. This mechanism predicts that  $\text{RhCH}_2^+$  should dominate over  $\text{RhCHD}^+$ , as is observed.

Reactions of  $\text{RhCH}_2^+$  with ethane are simpler than that for methane with reactions 6 and 7 observed.  $\text{RhCD}_2^+$  yields complete loss of label upon reaction with ethane. Formation of  $\text{RhC}_2\text{H}_4^+$  proceeds by addition of ethane to form **11** in analogy to the addition of methane in Scheme I. This is followed by a  $\beta$ -hydride



(65) (a) Since submitting this paper,  $\text{Nb}^+$  and  $\text{Ta}^+$  have been found to react with methane in the gas phase to yield  $\text{NbCH}_2^+$  and  $\text{TaCH}_2^+$ , respectively. Buckner, S. W.; MacMahon, T. J.; Freiser, B. S., unpublished results. (b) An anionic metal-carbene complex has also been reported to react with methane in the gas phase. Baumgartner, E.; Rhyne, T. C.; Dillard, J. G. *J. Organomet. Chem.* **1979**, *171*, 387.

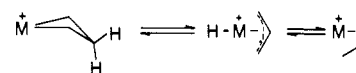
(66) Previously, kinetically excited atomic transition metal ions have been observed to react with methane. See, for example, ref 28.

(67) Halle, L. F.; Crowe, W. E.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1984**, *3*, 1694.

(68) (a) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (b) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Strille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

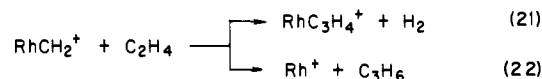
(69) Balazs, H. C.; Johnson, K. H.; Whitesides, G. M. *Inorg. Chem.* **1982**, *21*, 2162.

Scheme II



abstraction with subsequent reductive elimination of methane. Absence of H/D scrambling with  $\text{RhCD}_2^+$  indicates that  $\beta$ -hydride abstraction is much more facile than  $\alpha$ -hydride abstraction in **11**.

**Reactions with Ethene, Propene, and Cyclopropane.** Ethene reacts rapidly with  $\text{RhCH}_2^+$  to yield both dehydrogenation as well as  $\text{Rh}^+$  formation, reactions 21 and 22.  $\text{C}_3\text{H}_6$  is probably elim-

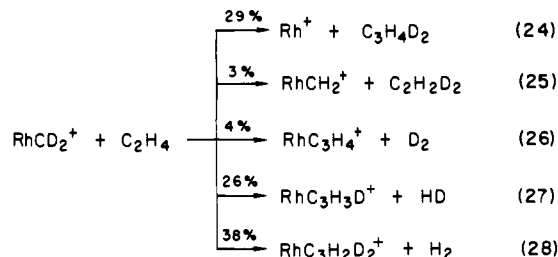


inated as propene since cyclopropane elimination is endothermic by  $\sim 9 \text{ kcal/mol}$ .<sup>44</sup> Both  $\text{RhC}_3\text{H}_4^+$  ions produced in reactions 2 and 21 undergo 4 H/D exchanges with deuterium. Furthermore, collisional activation of both  $\text{RhC}_3\text{H}_4^+$  ions yields predominantly  $\text{C}_3\text{H}_4$  elimination with a small amount ( $\sim 3\%$ ) of  $\text{RhC}^+$  formation at high kinetic energy. Therefore, both  $\text{RhC}_3\text{H}_4^+$  ions produced in reactions 2 and 21 are concluded to have identical structures. In addition,  $\text{RhC}_3\text{H}_4^+$  formed in reaction 23 behaves identically with the above  $\text{RhC}_3\text{H}_4^+$  ions with  $\text{D}_2$  as well as upon collisional



activation. Hence, it appears that  $\text{RhCH}_2^+$  coordinates ethene followed by rearrangement to a rhodacyclobutane. This is followed by rearrangement to a coordinated propene complex by  $\beta$ -hydride elimination which either eliminates propene or undergoes dehydrogenation. The rearrangement of metallacyclobutanes to coordinated olefins via hydride- $\pi$ -allyl intermediates is well supported in solution-phase studies.<sup>70-73</sup>

The strong  $\text{Rh}^+-\text{CH}_2$  bond strength should facilitate olefin metathesis since fewer side reactions are possible.<sup>3-7</sup> Reaction of  $\text{RhCD}_2^+$  with ethene, however, only yields 3%  $\text{RhCH}_2^+$  (the metathesis product) with formation of  $\text{Rh}^+$  and dehydrogenation products accounting for the remaining 97% of the product distribution, reactions 24–28. Recent calculations suggest that there



is no activation barrier for the interconversion of metallacyclobutanes to the corresponding olefin-alkylidene species.<sup>74</sup> The above results, therefore, indicate that  $\beta$ -hydride abstraction from the rhodacyclobutane ions is facile compared with elimination of ethene.

The degree of puckering of the metallacyclobutane ring is believed to be important for facile  $\beta$ -hydride abstraction, Scheme II.<sup>75</sup> The smaller the dihedral angle (greater puckering), the more favorable hydride transfer becomes. Hence, the rhodacyclobutane

(70) Tulip, T. H.; Ibers, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 4201.

(71) (a) Cushman, B. M.; Brown, D. B. *J. Organomet. Chem.* **1978**, *152*, C42. (b) Johnson, T. H.; Cheng, S. *J. Am. Chem. Soc.* **1979**, *101*, 5277.

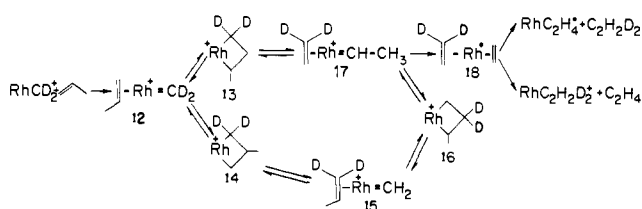
(72) (a) Ephritikhine, M.; Green, M. L. H.; MacKenzie, R. E. *J. Chem. Soc., Chem. Commun.* **1976**, 619. (b) Adam, G. J. A.; Davies, S. E.; Ford, K. A.; Ephritikhine, M.; Todd, P. F.; Green, M. L. H. *J. Mol. Catal.* **1980**, *15*.

(73) (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521. (b) Young, G. B.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 5808.

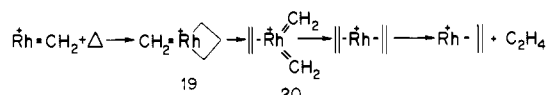
(74) Rappe, A. K.; Upton, T. H. *Organometallics* **1984**, *3*, 1440.

(75) Grubbs, R. H. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1982; Vol. 8, p 533.

Scheme III

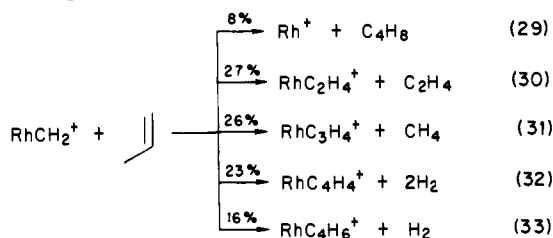


Scheme IV



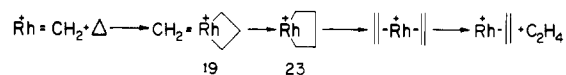
ions may have significant puckering. Recently, a stable rhodacyclobutane complex, (MCp)(PMe<sub>3</sub>)Rh(CH<sub>2</sub>)<sub>3</sub> (MCp = pentamethylcyclopentadienyl), was synthesized, and X-ray diffraction revealed that the rhodacyclobutane ring is essentially planar and symmetrical about the Rh-C<sub>1,2</sub> axis.<sup>76</sup> Therefore, the geometry of the rhodacyclobutane rings appears to vary considerably between the highly coordinatively unsaturated gas-phase species and the coordinatively saturated species. These differences, however, have been observed for other systems. For example, a nickelacyclobutane in solution appears to be in equilibrium with the olefin-coordinated nickel-carbene complex.<sup>77</sup> The corresponding nickelacyclobutane ions in the gas phase, however, undergo facile conversion to a Ni(propene)<sup>+</sup> complex via β-hydride elimination with no evidence for the nickelacyclobutane/ethene-carbene-nickel equilibrium.<sup>49,78</sup>

Reaction with propene yields reactions 29–33. Structural studies on RhC<sub>2</sub>H<sub>4</sub><sup>+</sup> formed in reaction 30 indicate it consists of



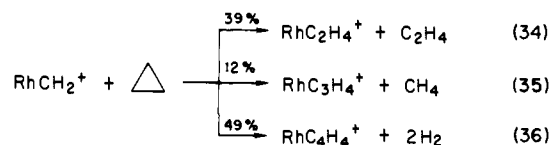
ethene bound to Rh<sup>+</sup>. With RhCD<sub>2</sub><sup>+</sup> roughly equal amounts of RhC<sub>2</sub>H<sub>4</sub><sup>+</sup> and RhC<sub>2</sub>H<sub>2</sub>D<sub>2</sub><sup>+</sup> are formed with no RhC<sub>2</sub>H<sub>3</sub>D<sup>+</sup> observed. These products correspond to metathesis processes. A mechanism for formation of these metathesis products is presented in Scheme III for RhCD<sub>2</sub><sup>+</sup>. Initially, the olefin coordinates to the carbene to form an activated complex, **12**, which is in equilibrium with the metallacyclobutane species **13** and **14**. The metallacyclobutane, **14**, can rearrange to the carbene species **15**, which, in turn, is in equilibrium with the metallacyclobutane species **14** and **16**. The metallacyclobutane complexes **13** and **16** can generate **17**, an ethylidene-ethene complex. Since there is little or no barrier for rearrangement of metallacyclobutanes to their corresponding olefin-alkylidene species,<sup>74</sup> intermediates **12** and **16** are believed to be in rapid equilibrium. Formation of the ethylidene species **17**, however, is followed by rapid and irreversible conversion to a coordinated ethylene. Complex **18** can then eliminate either C<sub>2</sub>H<sub>4</sub> or C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>. It is this ethylidene to ethylene rearrangement which accounts for the significant increase in metathesis of propene over ethene. Similar arguments have been put forth to explain this same observation for FeCH<sub>2</sub><sup>+</sup> and CoCH<sub>2</sub><sup>+</sup>.<sup>27a</sup> Finally, rearrangement of alkylidene species to coordinated olefins has been observed previously in solution and is a termination reaction in olefin metathesis.<sup>79,80</sup> Such a rear-

Scheme V



angement has also been reported to be facile for cationic alkylidene complexes.<sup>81</sup>

Reaction of cyclopropane with RhCH<sub>2</sub><sup>+</sup> yields three products, reactions 34–36. Structural studies indicate formation of Rh-



(ethene)<sup>+</sup> in reaction 34. A mechanism for formation of this product is presented in Scheme IV and involves initial insertion across the strain weakened C–C bond of cyclopropane forming an activated methylidene-metallacyclobutane species **19**. Cleavage of the metallacyclobutane ring generates the bis(methylidene)-ethene complex **20**. Coupling of the methylenes generates a bis(ethene) complex which eliminates ethene.

Theoretical studies suggest that there is little or no barrier for bis(methylene) to ethene interconversion for “allowed” reactions.<sup>82</sup> In addition, bis(carbene) complexes have been synthesized from **21**<sup>83</sup> and **22**<sup>84</sup> and stable bis(alkylidene) complexes have also been



prepared and studied.<sup>85,86</sup> In addition, methylidene coupling to form ethene has been observed in solution.<sup>87</sup> Finally, rhodacyclobutanes do interconvert rapidly with the corresponding methylene-ethene complex vide supra. Therefore, there is considerable precedent for the above mechanism of RhC<sub>2</sub>H<sub>4</sub><sup>+</sup> formation.

An alternative mechanism for RhC<sub>2</sub>H<sub>4</sub><sup>+</sup> formation in reaction 34 is presented in Scheme V and involves initial incorporation of methylene into the metallacyclobutane ring to generate the ring expansion product **23**, a metallacyclopentane. This metallacyclopentane then decomposes by symmetric ring cleavage followed by ethene elimination. Metallacyclopentanes decompose in solution by symmetric ring cleavage, resulting in formation of ethene, as well as by β-hydride elimination producing butene, and by reductive elimination of cyclobutane.<sup>4,88–92</sup> Metallacyclopentane

(80) Schrock, R. R. “Inorganic Chemistry: Towards the 21st Century”; American Chemical Society: Washington, D.C., 1983; ACS Symposium Series 211, Chapter 25.

(81) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761.

(82) Hoffmann, R.; Wilken, C. N.; Eisenstein, O. *J. Am. Chem. Soc.* **1982**, *104*, 632.

(83) (a) Cetinkaya, B.; Dixneuf, P.; Lappert, M. F. *J. Am. Chem. Soc., Dalton Trans.* **1974**, 1827. (b) Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1978**, 837 and references therein.

(84) (a) Ofele, K.; Herberhold, M. *Angew. Chem.* **1970**, 775. (b) Kreiter, C. G.; Ofele, K.; Wieser, G. W. *Chem. Ber.* **1976**, *109*, 1749.

(85) (a) Churchill, M. R.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1978**, 1048. (b) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1930.

(86) (a) Fellman, J. D.; Rupprecht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 5964. (b) Fellman, J. D.; Rupprecht, G. A.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5099.

(87) (a) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811. (b) Kegley, S. E.; Brookhardt, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760.

(88) (a) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 2418. (b) Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. L. *J. Am. Chem. Soc.* **1977**, *99*, 3863. (c) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7416.

(89) (a) Braterman, P. S. *J. Chem. Soc., Chem. Commun.* **1979**, 70. (b) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952. (c) McKinney, R. J.; Thorn, D. L.; Hoffmann, R.; Stockis, A. *J. Am. Chem. Soc.* **1981**, *103*, 2595.

(90) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.

(91) Diversi, P.; Ingrosso, G.; Lucherini, A. *J. Am. Chem. Soc.* **1978**, 735.

(76) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7272.

(77) Miyashita, A.; Grubbs, R. H. *Tetrahedron Lett.* **1981**, 22, 1255.

(78) Jacobson, D. B.; Freiser, B. S. *Organometallics* **1984**, *3*, 513.

(79) (a) Casey, C. P.; Loren, D. A.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2533. (b) Schrock, R. R.; Sharp, P. R. *J. Organomet. Chem.* **1979**, *171*, 43. (c) Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157.

ions (Fe, Co, Ni) decompose in the gas phase upon collisional activation both by symmetric ring cleavage ( $C_2H_4$  elimination) and by dehydrogenation.<sup>29,78,88,89,93,94</sup> In addition,  $Rh^+$  reacts with cyclobutane to generate  $RhC_2H_4^+$  as one of the products, presumably by symmetric ring cleavage of an activated rhodacyclopentane species.<sup>30</sup> Finally, the reverse of the above ring expansion process ( $\alpha$ -C-C bond cleavage) has been observed for nickelacyclohexanes in solution.<sup>95</sup> Hence, there is support for the ring expansion mechanism as well. It is quite likely, therefore, that both Schemes IV and V play a role in  $RhC_2H_4^+$  formation in reaction 34.

### Conclusions

The gas-phase chemistry of  $RhCH_2^+$  is much richer than that for either  $FeCH_2^+$  or  $CoCH_2^+$ .<sup>27</sup> For example,  $RhCH_2^+$  reacts readily with both dihydrogen and methane, whereas the corresponding  $FeCH_2^+$  and  $CoCH_2^+$  species are inert. In addition,  $RhCH_2^+$  yields additional products with both ethene and propene which are not observed for  $FeCH_2^+$  and  $CoCH_2^+$ .

(92) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4451.

(93) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6628.

(94) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.

(95) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7418.

The methylene bond strength,  $D^\circ(Rh^+-CH_2)$ , was bracketed between 92 and 95 kcal/mol from which  $D^\circ(Rh^+-CH_2) = 94 \pm 5$  kcal/mol is assigned. Structural studies clearly indicate that  $RhCH_2^+$  consists of a methylidene-rhodium complex, **1**, instead of a hydrido-methylidyne species, **2**. In contrast, thermodynamic considerations suggest that  $RhCH_3^+$  consists of a hydrido-methylidene complex, **4**, rather than the methyl species, **5**. In addition,  $\alpha$ -hydride abstraction from  $(CH_3)_2Rh^+$  appears to be quite facile. The activation barrier for reductive elimination of methane from  $Rh(H)(CH_3)^+$  appears to be less than 5 kcal/mol.

The strong  $Rh^+-CH_2$  bond should facilitate olefin methathesis; however, only a small amount is observed. The competing process for olefin metathesis is the facile rearrangement of rhodacyclobutane ion to coordinated propene by  $\beta$ -hydride elimination. This suggests that there is considerable puckering in the unsaturated rhodacyclobutane ring which favors  $\beta$  elimination.

In summary,  $RhCH_2^+$  is a very reactive species in the gas phase. The limited results here clearly indicate that further work in this area is warranted.

**Acknowledgment** is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-AC02-80ER10689) for supporting this research and the National Science Foundation (CHE-8310039) for providing funds for the advancement of FTMS methodology.

## Reactions of $FeCH_3^+$ and $CoCH_3^+$ with Aliphatic Alkenes and Alkynes in the Gas Phase

D. B. Jacobson<sup>†</sup> and B. S. Freiser\*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received February 25, 1985

**Abstract:** The gas-phase reactions of  $FeCH_3^+$  and  $CoCH_3^+$  with a variety of alkenes and alkynes are described by using Fourier transform mass spectrometry (FTMS).  $FeCH_3^+$  is unreactive with ethene, while  $CoCH_3^+$  reacts with ethene to yield the allyl product  $CoC_3H_5^+$ . This reaction presumably proceeds by initial methyl migratory insertion into coordinated ethene to form a  $Co(\text{propyl})^+$  complex which subsequently dehydrogenates. Reactions with alkenes containing labile hydrogens  $\alpha$  to the double bond proceed by initial elimination of methane to form an activated  $\pi$ -allyl complex which may subsequently decompose further. Both  $FeCH_3^+$  and  $CoCH_3^+$  undergo migratory insertion into coordinated butadiene generating a  $\pi$ -pentenyl complex which undergoes dehydrogenation. In addition, both  $FeCH_3^+$  and  $CoCH_3^+$  appear to insert into ethyne, generating a vinyl species which dehydrogenates to form  $MC_3H_3^+$ . These results suggest the following order for methyl migratory insertion into C-C multiple bonds: butadiene  $\sim$  ethyne  $>$  ethene. Decomposition of  $M(C_5H_9)^+$  species proceeds by initial skeletal rearrangement to a linear structure followed by dehydrocyclization to generate M-c- $C_5H_5^+$ . A stable  $Co(\text{pentadienyl})^+$  species was generated and is distinguishable from the corresponding  $Co(\text{cyclopentenyl})^+$  complex by H/D exchange with deuterium. Finally,  $D^\circ(Fe^+-\text{pentadienyl})$  is found to exceed  $70 \pm 6$  kcal/mol and  $D^\circ(Co^+-\text{pentadienyl})$  exceeds  $62 \pm 5$  kcal/mol.

Transition-metal alkyls<sup>1</sup> have been proposed as intermediates in a variety of important catalytic processes. For this reason transition-metal alkyls have been used as model compounds for homogeneous catalysis.<sup>2</sup> A particularly important process involving metal alkyls is the migratory insertion into carbon-carbon multiple bonds. For example, the catalytic arylation,<sup>3</sup> oligomerization,<sup>4</sup> Ziegler-Natta polymerization,<sup>5</sup> and (in some cases) carboalkoxylation<sup>6</sup> of olefins are believed to involve the insertion of metal-alkyl bonds into C-C double bonds. In addition, the catalytic trimerization<sup>7,8</sup> and (again, in some cases) the carboalkoxylation<sup>6</sup> of acetylenes are postulated to involve the insertion of metal-alkyl bonds into C-C triple bonds.

Due to the importance of these catalytic reactions, considerable effort has been devoted to the search for stoichiometric systems

in which such insertions can be observed directly and studied. One such process which, though intensely investigated, still remains

(1) (a) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243. (b) Davidson, D. P.; Lappart, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219. (c) Parshall, G. W.; Mrowca, J. J. *Adv. Organomet. Chem.* **1968**, *7*, 157. (d) Churchill, M. R. "Perspectives in Structural Chemistry"; Dunlavy, J. D., Ibers, J. A., Eds.; Wiley: New York, 1970; Vol. 3, p 91. (e) Braterman, P. S.; Cross, R. J. *Chem. Soc. Rev.* **1973**, *2*, 271.

(2) Klein, H.-F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 362 and references therein.

(3) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146 and references therein.

(4) (a) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337. (b) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (c) Soto, J.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 4479 and references therein.

(5) (a) Ballard, D. G. H. *J. Polym. Sci.* **1975**, *13*, 2191 and references therein. (b) Boor, J. "Ziegler-Natta Catalysts and Polymerizations"; Academic Press: New York, 1979. (c) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (d) Pino, P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 857.

<sup>†</sup>Current address: Department of Chemistry, California Institute of Technology, Pasadena, California 91125.