

$\text{Fe}(\text{H}_2\text{O})_6^{3+}$ . The latter is in good agreement with the X-ray scattering results<sup>29</sup> for iron(3+) perchlorate solution,  $\sigma_i \sim 0.055(5)$  Å.

One may derive  $\sigma_{\text{vib}}$  values from the Raman frequencies,  $\nu$ , from the relation shown in eq 5, in which  $\mu$  is the reduced mass. With

$$\sigma_{\text{vib}}^2 = \frac{h\nu}{8\pi^2\mu\nu} \coth\left(\frac{h\nu}{2kT}\right) \quad (5)$$

the vibrational frequencies for crystals used by Sutin,<sup>16</sup> we obtain  $\sigma_{\text{vib}}$  values of 0.0233 and 0.0194 Å, corresponding to the totally symmetric stretching modes for the Fe-O bonds in  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ , respectively, at room temperature.<sup>35</sup> These  $\sigma$  values are small compared with the EXAFS  $\sigma_i$  values, not a surprising result since  $\sigma_i$  includes all the vibrational modes. It is interesting to note that the  $r_2 - r^*$  and  $r^* - r_3$  differences, 0.065 and 0.040 Å, respectively are greater than the  $\sigma_{\text{vib}}$  values for the totally symmetric vibration, indicating that electron transfer requires much greater activation energy than the energy present on the average in the breathing motions of the complexes at room temperature.

**Acknowledgments.** We thank Drs. N. Sutin, M. Newton, and S. Heald for discussions and M. Chou for preparing some of the samples. We thank Dr. B. K. Teo for sending us some preprints prior to their publication. EXAFS spectra were measured at the Stanford Synchrotron Radiation Laboratory, which is supported by the National Science Foundation (under Contract DMF77-27489), in cooperation with SLAC and DOE. Work at Brookhaven National Laboratory was performed under the auspices of the Department of Energy.

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### Proton-Induced Ring Opening of a Dimetallacyclopropane-Type $\mu$ -Methylene-rhodium Compound. A Straightforward Novel Route to Halo(methyl) Complexes<sup>1</sup>

Sir:

Transition-metal methylene complexes containing unsubstituted metal-to-metal methylene ( $\text{CH}_2$ ) bridges have attracted considerable attention since the first examples of this class of compounds were reported in 1975.<sup>2</sup> Although they meanwhile have been thoroughly investigated by spectroscopic methods,<sup>3,4</sup> X-ray<sup>4a,5,6</sup>

(1) Transition Metal Methylene Complexes, 13. This work is being supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Degussa (Hanau), and the Hoechst Aktiengesellschaft. Part 12: W. A. Herrmann, J. Plank, and D. Riedel, *J. Organomet. Chem.*, **190**, C 47 (1980).

(2) W. A. Herrmann, B. Reiter, and H. Biersack, *J. Organomet. Chem.*, **97**, 245 (1975).

(3) For a recent review, see: W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, **17**, 800 (1978).  $\mu$ -Methylene transition-metal complexes will be covered in full detail in a forthcoming review article; cf.: W. A. Herrmann, *Adv. Organomet. Chem.*, in press.

(4) (a) M. Creswick, I. Bernal, and W. A. Herrmann, *J. Organomet. Chem.*, **172**, C39 (1979), and references cited therein; (b) K. K. Mayer and W. A. Herrmann, *ibid.*, **182**, 361 (1979); (c) R. J. Lawson and J. R. Shapley, *Inorg. Chem.*, **17**, 2963 (1978).

(5) (a) W. A. Herrmann, C. Krüger, R. Goddard, and I. Bernal, *Angew. Chem., Int. Ed. Engl.*, **16**, 334 (1977); (b) *J. Organomet. Chem.*, **140**, 73 (1977).

(6) (a)  $\mu\text{-CH}_2[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2]$ : R. B. Calvert, J. R. Shapley, A. J. Schultz, J. M. Williams, S. L. Suib, and G. D. Stucky, *J. Am. Chem. Soc.*, **100**, 6240 (1978); A. J. Schultz, J. M. Williams, R. B. Calvert, J. R. Shapley, and G. D. Stucky, *Inorg. Chem.*, **18**, 319 (1979). For the preparation and spectroscopic data of this compound, see also: R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, **99**, 5225 (1977); *ibid.*, **100**, 6544 (1978). (b)  $\mu\text{-CH}_2\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2$ : T. F. Koetzle, F. Takusagawa, A. Fumagalli, and W. A. Herrmann, *Inorg. Chem.*, submitted for publication.

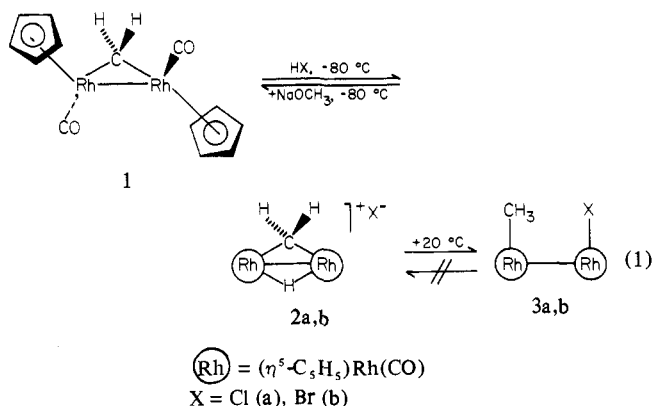
Table I. Selected Bond Lengths and Angles of 3b<sup>a</sup>

bond lengths, pm		bond angles, deg	
Rh(1)-Rh(2)	266.0 (3)		
Rh(1)-Br <sup>a</sup>	250.4 (13)	C(2)-Rh(1)-Rh(2)	102.3 (13)
Rh(2)-Br <sup>a</sup>	254.1 (6)	C(1)-Rh(1)-Rh(2)	48.1 (6)
Rh(1)-C(1)	199.5 (20)	C(1)-Rh(1)-C(1')	91.1 (11)
Rh(2)-C(1')	199.3 (20)	Rh(1)-C(1)-Rh(2)	83.7 (9)
Rh(2)-C(2) <sup>a</sup>	234.1 (48)	Rh(1)-C(1)-O(1)	137.7 (15)
Rh(1)-C(2) <sup>a</sup>	248.6 (54)	Rh(2)-C(1)-O(1)	138.6 (15)
Rh(1)-C(4)	228.8 (32)	C(5)-C(4)-C(5')	104.6 (26)
Rh(1)-C(5)	229.5 (21)	C(4)-C(5)-C(6)	111.2 (20)
Rh(1)-C(6)	222.3 (16)	C(5)-C(6)-C(6')	106.1 (12)
Rh(2)-C(7)	208.4 (38)	Br-Rh(2)-Rh(1)	100.3 (1)
Rh(2)-C(8)	217.8 (38)	C(1)-Rh(2)-Rh(1)	48.2 (6)
Rh(2)-C(9)	222.4 (25)	C(1)-Rh(2)-C(1')	91.3 (12)
C(4)-C(5)	142.4 (29)	C(8)-C(7)-C(8')	108.1 (47)
C(5)-C(6)	144.5 (31)	C(7)-C(8)-C(9)	108.1 (36)
C(6)-C(6')	145.0 (41)	C(8)-C(9)-C(9')	107.7 (23)
C(7)-C(8)	123.2 (45)		
C(8)-C(9)	130.2 (48)		
C(9)-C(9')	120.4 (69)		

<sup>a</sup> The positions of C(2) and Br are statistically disordered.

as well as neutron-diffraction techniques,<sup>6</sup> Hückel MO calculations,<sup>7</sup> and a representative experimental electron density determination,<sup>8</sup> very little is known about their chemistry to date. Both photochemically and thermally remarkably stable and also synthetically easily available, the dinuclear  $\mu$ -methylene-rhodium complex  $\mu\text{-CH}_2[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2$  (**1**)<sup>5</sup> represents a neat example of the dimetallacyclopropane-type compounds structurally characterized by a methylene function which bridges a pronounced electron-rich metal-metal bond. Recently, we demonstrated that strong protic acids such as tetrafluoroboric acid initiate clean clusterification of **1**, yielding novel trinuclear  $\mu_3$ -methylidene derivatives of high thermal stability.<sup>9</sup> Bearing the obvious catalytic importance of simple, metal-bound hydrocarbon fragments and their mechanistic fate in mind,<sup>10</sup> we now report, for the first time, on the proton-induced ring opening of the three-membered Rh-CH<sub>2</sub>-Rh skeleton of **1** and the molecular structure of the final product.

If the  $\mu$ -methylene-rhodium complex **1** is allowed to react with dry hydrogen halides such as HCl or HBr, brown, slightly air-sensitive, neutral compounds **3a** and **3b**, respectively, are quickly formed according to eq 1 in near quantitative yields.<sup>11</sup> In a typical

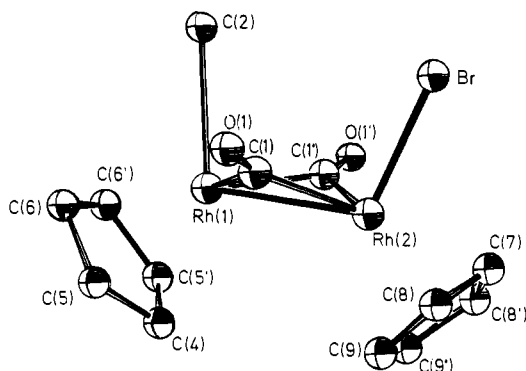


(7) P. Hofmann, *Angew. Chem., Int. Ed. Engl.*, **18**, 554 (1979); in this context, see also: A. R. Pinhas, T. A. Albright, P. Hofmann, and R. Hoffmann, *Helv. Chim. Acta*, **63**, 29 (1980).

(8) D. A. Clemente (C.N.R. Padova/Italy), unpublished work on  $\mu\text{-CH}_2[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2$ ,<sup>2</sup> 1978-1980.

(9) W. A. Herrmann, J. Plank, E. Guggolz, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, in press.

(10) For a recent review, see: E. L. Muetterties and J. Stein, *Chem. Rev.*, **79**, 479 (1979).



**Figure 1.** ORTEP representation of bromo(methyl)bis[( $\mu$ -carbonyl)( $\eta^5$ -cyclopentadienyl)rhodium] (*Rh-Rh*) (**3b**). The thermal ellipsoids correspond to 50% probability. Since the bromo and the methyl carbon atoms are statistically distributed, only one position of each is shown for clarity.

experiment, a vigorously stirred solution of 406 mg (1.0 mmol) of **1** in 10 mL of diethyl ether was dropwise treated with 2 mL (excess) of a saturated solution of dry HBr gas in the same solvent at room temperature. The powdery precipitate, which immediately occurs, originally has a light yellow color, gradually changing to dark brown upon further addition of HBr. After all of the acid has been added, the precipitate **3b** is quickly collected on a D3 frit, washed a few times with 5-mL portions of ether, and finally crystallized from a nearly saturated solution in methylene chloride ( $-35$  to  $-78$  °C); yield 463 mg (95%); dec  $>138$  °C (sealed capillary).

Although the spectroscopic data strongly indicated dinuclear structures containing two cyclopentadienylrhodium fragments linked together by two carbonyl groups both in solution and in the crystalline state,<sup>11</sup> we decided to undertake a single-crystal X-ray-diffraction study of the bromo derivative **3b** in order to unequivocally determine its structure. This compound crystallizes from methylene chloride (crystal size 0.35 mm  $\times$  0.35 mm  $\times$  0.40 mm) in the centric space group  $D_{2h}^{16}$ -*Pm**cn*<sup>12</sup> with the cell parameters  $a = 890.7$  (2),  $b = 1016.8$  (2),  $c = 1567.1$  (3) pm;  $\alpha = 89.87$  (2),  $\beta = 90.07$  (2),  $\gamma = 90.00$  (2) $^\circ$ ;  $V = 1419.29 \times 10^6$  pm<sup>3</sup>;  $Z = 4$ . A total of 1050 independent, nonzero reflections [ $I > 2.5\sigma(I)$ ] were recorded with an automatic, computer-controlled four-circle Siemens diffractometer ( $60^\circ \geq 2\theta \geq 0^\circ$ ; Mo K $\alpha$  irradiation; molar absorption coefficient 50.71 cm<sup>-1</sup>). The structure was solved and refined by standard methods ( $R_{\text{iso}} = 8.08\%$ ,  $R_{\text{anis}} = 6.87\%$ ) and proved to be in perfect agreement with the IR and <sup>1</sup>H NMR spectroscopic evidence. An ORTEP representation is given in Figure 1. Some relevant bond distances and angles are found in Table I.

The basic geometry of the  $C_2$ -symmetric molecule is characterized by a short rhodium-rhodium bond which is symmetrically bridged by two carbonyl groups.<sup>13</sup> Strikingly, the four-membered

(11) Anal. Calcd for  $C_{13}H_{13}ClO_2Rh_2$  (442.5): C, 35.29; H, 2.96; Cl, 8.01; Rh, 46.51. Found for **3a**: C, 35.04; H, 3.12; Cl, 7.78; Rh, 46.61. Calcd for  $C_{13}H_{13}BrO_2Rh_2$  (487.0): C, 32.07; H, 2.69; Br, 16.41; Rh, 42.26. Found for **3b**: C, 32.18; H, 2.84; Br, 16.49; Rh, 42.63. IR ( $\nu_{\text{CO}}$ , cm<sup>-1</sup>): **3a** (KBr) 1878 (w), 1843 (st); (CH<sub>2</sub>Cl<sub>2</sub>) 1890 (w), 1847 (vst); **3b** (KBr) 1879 (w), 1844 (st); (CH<sub>2</sub>Cl<sub>2</sub>) 1892 (w), 1849 (vst). <sup>1</sup>H NMR (90 MHz, CD<sub>2</sub>Cl<sub>2</sub>, int. Me<sub>4</sub>Si, 25 °C): **3a** (X = Cl),  $\tau$  C<sub>5</sub>H<sub>5</sub> 4.37 [m(2"dd)], 10 H;  $^2J_{\text{Rh,H}}$  ca. 0.6 Hz],  $\tau$  CH<sub>3</sub> 9.55 [d, 3 H;  $^2J_{\text{Rh,H}} = 2.5$  Hz]; **3b** (X = Br),  $\tau$  C<sub>5</sub>H<sub>5</sub> 4.33 [m(2"dd)], 5 H;  $^2J_{\text{Rh,H}} = 0.60$  Hz], 4.37 [m(2"dd)], 5 H;  $^2J_{\text{Rh,H}} = 0.75$  Hz],  $\tau$  CH<sub>3</sub> 9.51 [d, 3 H;  $^2J_{\text{Rh,H}} = 2.5$  Hz]. Conductivity (CH<sub>3</sub>NO<sub>2</sub>; 21.6 °C;  $4.0 \times 10^{-4}$  M): **3a**,  $\Lambda = 1.4$  cm<sup>2</sup>mol<sup>-1</sup>Ω<sup>-1</sup>; **3b**,  $\Lambda = 1.5$  cm<sup>2</sup>mol<sup>-1</sup>Ω<sup>-1</sup>. Note, however, that these values were obtained from freshly prepared solutions under vigorous exclusion of air and water; upon standing for a few hours, the solutions show significantly higher conductivity ( $\Lambda$  ca. 5 cm<sup>2</sup>mol<sup>-1</sup>Ω<sup>-1</sup>) which, very likely, is due to some decomposition caused by the solvent. Similarly, weak absorptions for terminal CO ligands [e.g., **3b** (CH<sub>2</sub>Cl<sub>2</sub>) 1980, 2036 (sh), 2300 cm<sup>-1</sup>] begin to appear in the solution IR spectra after ca. 15 min at room temperature; temperature-dependent IR spectroscopy clearly demonstrates this effect *not* to be due to an isomerization phenomenon of the doubly CO-bridged complexes **3a** and **3b**.

(12) Systematic absences  $h0k$  ( $h + k = 2n + 1$ ) and  $h0l$  ( $l = 2n + 1$ ); Syntex P3 diffractometer program.

frame defined by the two metal atoms and the carbonyl carbons is not planar but tilted toward the terminal ligand sites (CH<sub>3</sub> and Br, respectively), the interplanar angle [Rh(1)-C(1)-Rh(2) vs. Rh(1)-C(1')-Rh(2)] amounting to 147.0 (10) $^\circ$ . The most interesting feature of this molecule, however, is its stereochemistry regarding the metal centers: although the methylene starting compound **1** ( $C_2$  symmetry) displays kinetically stable *S,S* (or *R,R*) configurations as regards the chiral rhodium centers, arising from trans-oriented sets of terminal ligands (C<sub>5</sub>H<sub>5</sub>; CO),<sup>5,14</sup> its ring-opening product **3b** exhibits both the cyclopentadienyl groups and the remaining terminal functions CH<sub>3</sub> and Br in *cis* position to each other, suggesting rotation of the CpRh fragments around a nonbridged metal-metal bond in the course of the reaction **1**  $\rightarrow$  **3b**.

In this context, we are in fact able to clearly answer the question as to when ring opening occurs; if the protonation reaction of **1** as described above is conducted at *low* temperatures ( $-80$  °C), a light yellow precipitate is formed which has been characterized as the cationic hydrido(methylene) species **2** by conductivity measurements (1:1 electrolyte) and chemical transformations.<sup>15</sup> For example, the initial product **2b** instantaneously is deprotonated by the action of sodium methoxide in methanol at  $-80$  °C, yielding authentic  $\mu$ -methylene precursor **1**. This reaction is completely consistent with our observations on the behavior of [( $\mu$ -H)( $\mu$ -CH<sub>2</sub>)]( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Rh(CO)<sub>2</sub><sup>+</sup>Y<sup>-</sup> (Y = CF<sub>3</sub>SO<sub>3</sub>, BF<sub>4</sub>, CF<sub>3</sub>CO<sub>2</sub>, FSO<sub>3</sub>) and [( $\mu$ -H)( $\mu$ -CO)]( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Rh(CO)<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup> reported earlier.<sup>19</sup> When the cationic hydrido(methylene) complex **2b** is warmed to room temperature it rapidly undergoes effective irreversible ring opening either in the solid state or in nitromethane solution, finally yielding the thermally stable bromo(methyl) derivative **3b**, initiated by coordination of the halide counterion (eq 1). Combination of the hydrido and the methylene bridges originally oriented trans to each other was shown to proceed via hydrido(methylene)/methyl tautomerism,<sup>9</sup> a process which was first established convincingly by Shapley et al. for Os<sub>3</sub>(CO)<sub>10</sub>(CH<sub>2</sub>)H<sub>2</sub>.<sup>6a</sup>

The reaction sequence outlined above not only provides the first authentic example of a ring-opening process of dimetallocyclopropane-type  $\mu$ -methylene complexes but also demonstrates that a nonsynchronous two-step mechanism which requires the prerequisite of proton-induced metal-to-metal bond activation is responsible for this kind of reaction.<sup>16</sup> The salient product-determining importance of the nucleophilic halide counterions is evident from comparison with the chemistry of hydrido(methylene) complexes containing anions which lack coordination capabilities; thus, the compound **2**-BF<sub>4</sub>, isolated in pure form as well, spontaneously forms [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Rh<sub>3</sub>( $\mu$ -CO)<sub>2</sub>( $\mu_3$ -CH)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> in 96% yield with concomitant elimination of hydrogen and methane.<sup>9</sup>

(13) The rhodium-rhodium separation [266.0 (3) pm] very much resembles the corresponding distances found for other di- or trinuclear cyclopentadienylrhodium complexes containing edge-bridging two-electron ligands (e.g., CO or CH<sub>2</sub>). By way of contrast, Rh-Rh distances considered to be nonbonding in character are quite long (e.g., 371.91 (6) pm for  $\mu$ -Cl<sub>2</sub>[(Me<sub>5</sub>C<sub>5</sub>)RhCl]<sub>2</sub>): M. R. Churchill, S. A. Julis, and F. Rotella, *Inorg. Chem.*, **16**, 1137 (1977).

(14) The only reasonable mechanism for epimerization of **1** involves carbonyl exchange, which is *not* observed NMR spectroscopically in toluene even at  $+90$  °C: F. A. Cotton, personal communication, 1979; see also, ref 4c and 17.

(15) Due to the instability of both **2a** and **2b** in regard to transformation to the nonionic halo(methyl) complexes **3a** and **3b**, respectively, reliable IR and <sup>1</sup>H NMR data, which were hoped to *cleanly* discriminate between the formulations ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Rh<sub>2</sub>(CO)<sub>2</sub>CH<sub>3</sub><sup>+</sup> and ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Rh<sub>2</sub>(CO)<sub>2</sub>(CH<sub>2</sub>)H<sup>+</sup>, could not be obtained. However, a high-field resonance ( $\tau$  23.2,  $^1J(\text{Rh,H}) = 22.8$  Hz, CD<sub>3</sub>NO<sub>2</sub>,  $-28$  °C) was observed for a freshly prepared sample of **2b** in the <sup>1</sup>H NMR spectra. Moreover, the intermediates **2a** and **2b** were converted by anion metathesis into the well-established BF<sub>4</sub> salt ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Rh<sub>2</sub>(CO)<sub>2</sub>(H)<sup>+</sup>BF<sub>4</sub><sup>-</sup> which was characterized by IR and <sup>1</sup>H NMR spectroscopy to be identical with an authentic sample (see ref 9). These results unequivocally demonstrate that the intermediates **2a** and **2b** are structurally analogous with the expectedly more stable primary protonation products obtained with acids such as HBF<sub>4</sub> instead of HCl and HBr, respectively.

(16)  $\mu$ -Methylene complexes without metal-metal bonds are protonated at the CH<sub>2</sub> bridge and do not show CH<sub>2</sub>(H)/CH<sub>3</sub> tautomerism: M. B. Hursthouse, R. J. Jones, K. M. Abdul Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, **101**, 4128 (1979).

In conclusion, ring opening of dimetallacyclopropanes of the type discussed in this communication points to a promising new synthetic entry to the hitherto little investigated class of dinuclear organometals having alkyl and halide groups bound to adjacent metal centers.<sup>17</sup> This simple preparative route and its mechanistic implications are presently under active investigation in our laboratories.

**Supplementary Material Available:** List of atomic, population, and thermal parameters of **3b** (1 page). Ordering information is given on any current masthead page.

(17) In this context, the reader's attention is drawn to related homodinuclear dimethyl complexes of type  $[(\mu\text{-CO})(\text{CH}_3)(\eta^2\text{-C}_3\text{H}_5)\text{Co}]_2$  reported by Bergman et al., which exhibit some fascinating decomposition pathways: I. E. Schore, C. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, **98**, 7436 (1976); H. E. Bryndza and R. G. Bergman, *ibid.*, **101**, 4766 (1979); M. A. White and R. G. Bergman, *J. Chem. Soc., Chem. Commun.*, 1056 (1979).

(18) Karl Winnacker Scholarship Recipient, 1979-1984.

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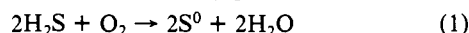
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*Received April 7, 1980*

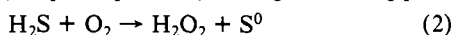
## Selective Reductions of Ammineruthenium(III) Complexes by Hydrogen Sulfide

Sir:

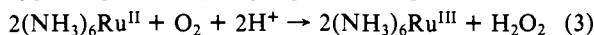
Due to more stringent pollution regulations, hydrogen sulfide is being recovered in increasing amounts. Hydrogen sulfide is an effective reducing agent, as exemplified by the Claus process<sup>1</sup> in which oxygen is reduced to water (eq 1). We have become



interested in a modification of this reaction which would allow us to use hydrogen sulfide for partial reduction of oxygen to hydrogen peroxide (compare eq 1 and 2). A logical starting point



for this chemistry is the observation by Taube and co-workers that ammineruthenium(II) complexes<sup>2</sup> serve as specific reducing agents for oxygen to produce hydrogen peroxide (eq 3).<sup>3</sup> It occurred



to us that it might be possible to reduce the oxidized ruthenium complexes with hydrogen sulfide without the incorporation of sulfur ligands since these complexes are nonlabile and coordinatively saturated. Herein we report our preliminary results in this area which demonstrate that hydrogen sulfide can indeed function as a selective and potent outer-sphere reductant for these coordinatively saturated complexes.

In a typical procedure  $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{py})_2(\text{S}_2\text{O}_6)_3]^4$  (py  $\equiv$  pyridine) is dissolved in deoxygenated water. Hydrogen sulfide is bubbled through the clear solution, resulting in an immediate color change to bright yellow. This transformation is accompanied by the formation of a fine, off-white precipitate which can be filtered.

(1) Gamson, B. W.; Elkins, R. H. *Chem. Eng. Prog.* **1953**, *49*, 203-215. Palm, J. W. *Hydrochem. Process.* **1972**, *51*(3), 105-108.

(2) All of the complexes discussed herein are cationic, containing six neutral ligands. The molecular formulas of the ruthenium(III) complexes (with the associated anions) are  $[(\text{NH}_3)_5\text{Ru}(\text{py})_2(\text{S}_2\text{O}_6)_3]$ ,  $[(\text{NH}_3)_4\text{Ru}(\text{py})_2(\text{ClO}_4)_3]$ ,  $[(\text{NH}_3)_4\text{Ru}(\text{bpy})](\text{PF}_6)_3$ ,  $[(\text{TMED})_2\text{Ru}(\text{bpy})](\text{PF}_6)_3$ ,  $[(\text{NH}_3)_3\text{Ru}(\text{OH}_2)](\text{CF}_3\text{SO}_3)_3$ , and  $[(\text{NH}_3)_6\text{Ru}]\text{Cl}_3$ .

(3) Pladziejewicz, J. R.; Meyer, T. J.; Broomhead, J. A.; Taube, H. *Inorg. Chem.* **1973**, *12*, 639-643. Stanbury, D. M.; Haas, O.; Taube, H. *ibid.* **1980**, *19*, 518-524.

(4) Ford, P.; Rudd, DeF. P.; Gaunders, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187-1194.

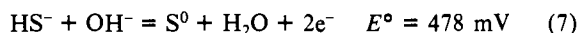
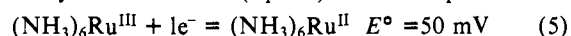
Analysis of this material shows it to be elemental sulfur. Examination of the filtrate by UV-vis spectroscopy reveals that a quantitative reduction of the ruthenium(III) complex to  $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{py})_2(\text{S}_2\text{O}_6)]$  has taken place. A solid can also be isolated by addition of excess anion. Microanalysis confirms it to be the expected ruthenium(II) complex. Overall, the reaction can be represented by eq 4.



The reduction proceeds equally well with  $(\text{NH}_3)_4\text{Ru}^{\text{III}}(\text{py})_2^5$  and  $(\text{NH}_3)_4\text{Ru}^{\text{III}}(\text{bpy})^6$  (bpy  $\equiv$  2,2'-bipyridine). Quantitative amounts of the corresponding ruthenium(II) complexes are formed in seconds. In the case of  $(\text{TMED})_2\text{Ru}^{\text{III}}(\text{bpy})^7$  [TMED  $\equiv$   $\text{NH}_2\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{NH}_2$ ], the reaction is much slower, on the order of hours to go to completion. This finding is corroborated by the fact that the same complex is slow to disproportionate into a mixture of the corresponding ruthenium(II) and ruthenium(IV) species.<sup>8</sup>

The reduction of the aquo complex  $(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{OH}_2)^9$  is also facile. The corresponding ruthenium(II) complex may be trapped quantitatively by isonicotinamide (ISN) to give  $(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{ISN})^{10}$ . If isonicotinamide is not present, the known hydrogen sulfide complex is formed.<sup>11</sup> In the presence of oxygen, this complex is rapidly oxidized to yield the well-characterized disulfide-bridged dimer  $[(\text{NH}_3)_5\text{RuS-SRu}(\text{NH}_3)_5]^{4+}$ .<sup>12</sup> Thus, sulfur incorporation can be avoided only if coordinatively saturated complexes are employed.

The pH dependence of the reduction can be demonstrated in reactions of hydrogen sulfide with hexaammineruthenium(III). In 0.1 M trifluoroacetic acid solution, no reduction takes place. On the basis of the potentials of the redox couples shown below, this is readily understandable (eq 5-7).<sup>13</sup> As the pH is raised



to approximately 4,  $(\text{NH}_3)_6\text{Ru}^{\text{II}}$  and elemental sulfur start to appear.

In preliminary attempts to define the scope and limitations of this reaction, it has been found that methyl mercaptan also reduces the pentaammineruthenium(III)-pyridine complex. In analogy to other oxidants, the oxidation product of methyl mercaptan is believed to be dimethyl disulfide.<sup>14</sup> The reaction is not as rapid as with hydrogen sulfide and proceeds to only approximately 70% completion.

Coordinatively saturated ferric complexes behave analogously to the ruthenium complexes. Thus, tris(*o*-phenanthroline)ferric ion is rapidly and quantitatively reduced to ferrous ion, and hy-

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(6) Alvarez, V. E.; Allen, R. J.; Matsubaru, T.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 7686-7692. The corresponding ruthenium(III) complex may be prepared by ceric oxidation of the ruthenium(II) complex.

(7) This complex was prepared by displacement of the ammonia ligands from  $(\text{NH}_3)_6\text{Ru}^{\text{III}}(\text{bpy})$  by TMED followed by ceric oxidation.

(8) The slow rates of reduction and disproportionation are anomalous in view of the fact that these complexes are expected to undergo an adiabatic electron transfer via the bipyridyl ligand. Thus, the rates of reduction of  $(\text{NH}_3)_4\text{Ru}^{\text{III}}(\text{bpy})$  and  $(\text{TMED})_2\text{Ru}^{\text{III}}(\text{bpy})$  are expected to be very similar. The discrepancy between the expected and observed behavior of  $(\text{TMED})_2\text{Ru}^{\text{III}}(\text{bpy})$  cannot be explained at this time. For disproportionation of other ruthenium(III) complexes, see: Rudd, DeF. P.; Taube, H. *Inorg. Chem.* **1971**, *7*, 1543-1544.

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(12) Bruet, C. R.; Isied, S. S.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 4758-4759.

(13) Note that the reduction potentials for the complexes containing aromatic nitrogen heterocycles are all greater than 300 mV. The overall reaction with hydrogen sulfide is highly favored. This is not true for the hexaammineruthenium(III) ion: Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460-1466. Matsubaru, T.; Ford, P. C. *ibid.* **1976**, *15*, 1107-1110.

(14) Many oxidizing agents are known to convert mercaptans to disulfides. See, for example: Collman, J. P.; Sorrell, T. N.; Hoffman, B. M. *J. Am. Chem. Soc.* **1975**, *97*, 913-914.