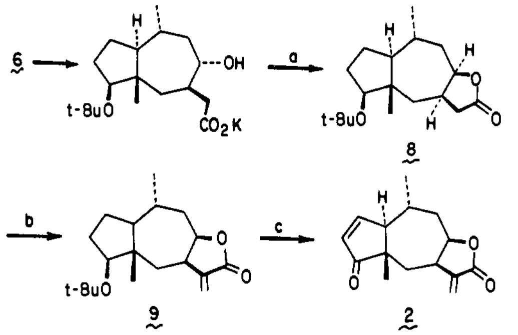
Scheme II[a]



[a](a) excess CH_3SO_2Cl, $(C_2H_5)_3N$, THF; aqueous NaOH; (b) Stiles reagent, then CH_2O, $(C_2H_5)_2NH$, CH_3CO_2H;[21] (c) Scheme I, steps g-i.

nation[15] (in 75% crude yield) provided crystalline (±)-**1**, mp 178-181 °C, which was identical in all respects except for optical rotation with authentic (+)-**1**, by TLC, ^1H NMR, IR and MS.[16]

Having rigorously characterized (±)-**1**, we returned to **6** and undertook regiospecific C-8 epimerization of the latter, to gain access to aromatin (**2**) as well (Scheme II). The dried potassium salt of hydrolyzed **6** (KOH-CH_3OH) was reacted with excess mesyl chloride and triethylamine in tetrahydrofuran (sulfene-generating conditions[17]), so as to favor C-8 *hydroxyl activation*,[18] necessary for inversion, at least competitively with carboxyl activation,[19] which normally predominates during arenesulfonylation[20] (and promotes lactonization with stereochemical retention[20]). The crude mixed anhydride-C-8 mesylate so produced was treated directly with aqueous sodium hydroxide, resulting in quantitative isolation of crude **8**:[6b] IR (neat) 1780, 1200 cm^{-1} (~85% inversion, based on NMR integration of C-8 proton signals, at δ 4.8 in **8** and 4.2 in **6**). The latter was treated with Stiles reagent, whereupon *un*carboxylated residual **6** was removed by extraction, followed by Mannich alkylation-decarboxylation according to Parker and Johnson.[21] The cis-fused methylenelactone **9**[6b] [mp 95-97 °C; IR (neat) 1760, 1660 cm^{-1}], preparable in 50% yield from **6** (three steps), was then converted into **2** using the same reactions[13,15] employed in the **7** → **1** transformation. During this series, crystalline 2,3-dihydroaromatin[6b] (2,3-dihydro-**2**) was obtained in high purity, mp 113-114 °C, and shown to be devoid of 2,3-dihydro-**1** (by NMR). The yield of (±)-**2**, mp 125-126 °C, was ~35% for five steps beginning with **9**, and the ^1H NMR spectrum was identical with that reported[3b] for (−)-**2**.

These accomplishments, with some steps yet to be refined, are cause for optimism in our continuing efforts to synthesize even more complex members of the fascinating pseudoguaianolide family and we shall report on these matters in due course.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-7720815) for financial support. Kevan Thompson and Thomas Nickson rendered valuable assistance in model studies and preparation of intermediates, respectively. Professor P. Joseph-Nathan kindly provided a sample of (+)-aromaticin. We also thank Dr. George Lee for aid in securing mass spectra and Dr. Stanley Sojka for FT IR and NMR spectra.

References and Notes

(1) Romo, J.; Joseph-Nathan, P.; Diaz, F. *Tetrahedron*, **1964,** *20*, 79-85.

(2) For recent accomplishments in the total synthesis of helenanolides, see: Ohfune, Y.; Grieco, P. A.; Wang, C.-L., J.; Majetich, G. *J. Am. Chem. Soc.* **1978,** *100*, 5946-5948. Grieco, P. A.; Ohfune, Y.; Majetich, G. *Tetrahedron Lett.* **1979,** *35*, 3265-3268. Grieco, P. A.; Ohfune, Y.; Majetich, G. *J. Org. Chem.* **1979,** *44*, 3092-3093. Roberts, M. R.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1979,** *101*, 7626-7627. Kok, P.; de Clerq, P. J.; Vande walle, M. E. *J. Org. Chem.* **1979,** *44*, 4553-4557.

(3) (a) Romo, J.; Romo de Vivar, A. *Fortschr. Chem. Org. Naturst.* **1967,** *25*, 90-130. (b) Yoshioka, H.; Mabry, T. J.; Timmerman, B. N. "Sesquiterpene Lactones"; University of Tokyo Press: Tokyo, 1973.

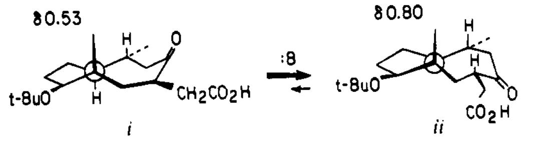
(4) Lansbury, P. T.; Serelis, A. K. *Tetrahedron Lett.* **1978,** *22*, 1909-1912.

(5) Lansbury, P. T.; Hangauer, D. G., Jr. *Tetrahedron Lett.* **1979,** *38*, 3623-3626.

(6) (a) Satisfactory elemental analyses and (b) ^1H NMR and infrared spectral data consistent with the assigned structure were obtained for this compound.

(7) Varech, D.; Jacques, J. *Bull. Soc. Chim. Fr.* **1969,** 3505-3515.

(8) The presumption that **6** possessed the proper relative configuration for preparing 1 was initially verified as follows. Ruthenum tetroxide oxidation (Lee, D. G.; van den Engh, M. In "Oxidation in Organic Chemistry", Trahanovsky, W. S., Ed.; Academic Press: New York, 1973; Part B, pp 177-227) of **5** or the cyclic ether derived from **5** via intramolecular alkoxide displacement upon the primary monotosylate gave not only the expected **6** (~40%) but also the keto acid i (~40%), mp 119-120 °C. Since the C-7 side chain in acid i would not epimerize during RuO_4 oxidation,[9] the only chair conformation that relieves diaxial compression between β-oriented substituents at C-5 and C-7 is that in which the C-5 methyl is highly shielded (δ 0.53 ppm). As anticipated, DBN epimerized i to the keto acid ii,[6b] mp



85-87 °C, whose α-oriented C-7 side chain allows population of the alternate chair conformation in which the C-5 methyl signal "shifts back" to δ 0.80 ppm.

(9) (a) Butterworth, R. F.; Overend, W. G.; Williams, N. R. *Tetrahedron Lett.* **1968,** 3239-3242. (b) Wheeler, J. W.; Oh, S. K.; Benfield, E. F.; Neff, S. E. *J. Am. Chem. Soc.* **1972,** *94*, 7589-7590. (c) Branca, S. J.; Smith, A. B., III *J. Org. Chem.* **1977,** *42*, 1026-1030.

(10) (a) Grieco, P. A. *Synthesis* **1975,** 67-82. (b) Danishefsky, S.; Kitahara, T.; McKee, R.; Schuda, P. F. *J. Am. Chem. Soc.* **1976,** *98*, 6715-6717. (c) Patterson, I.; Fleming, I. *Tetrahedron Lett.* **1979,** 993-996.

(11) Herrmann, J. L.; Schlessinger, R. H. *J. Chem. Soc., Chem. Commun.* **1973,** 711-712.

(12) Gassman, P. G.; Schenk, W. N. *J. Org. Chem.* **1977,** *42*, 918-920.

(13) Marshall, J. A.; Ellison, R. H. *J. Am. Chem. Soc.* **1976,** *98*, 4312-4313.

(14) Bohlmann, F.; Mahanta, P. K. *Phytochemistry* **1979,** *18*, 887-888.

(15) Grieco, P. A.; Ohfune, Y.; Majetich, G. *J. Am. Chem. Soc.* **1977,** *99*, 7393-7395.

(16) Experimental details for all stages in the synthesis of 1 are provided in the Ph.D. Dissertation of D. G. Hangauer, Jr., SUNY at Buffalo, 1980.

(17) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970,** *35*, 3195-3196.

(18) The DEADCAT reaction (cf. Trost, B. M.; Shuey, C. D.; DiNinno, F., Jr. *J. Am. Chem. Soc.* **1979,** *101*, 1284-1285) has found use for forming γ-butyrolactones with hydroxyl inversion when the functional groups are *geometrically prevented* from rapid lactonization. However, even when the potassium salt of hydrolyzed **6** is neutralized in situ, relactonization takes precedence over attempted DEADCAT reaction, and no detectable **8** is produced.

(19) It is likely that carboxylate attack on *sulfene*[17] is *reversible*, while attack on hydroxyl and zwitterion collapse via proton transfer is irreversible. This speculation seems valid, since mesylation in pyridine gives a 1:1 mixture of **8** and recovered **6**.

(20) Adam, W.; Baeza, J.; Liu, J.-C. *J. Am. Chem. Soc.* **1972,** *94*, 2000-2006.

(21) Parker, W. H.; Johnson, F. *J. Org. Chem.* **1973,** *38*, 2489-2496.

(22) Allied Chemical Corporation Predoctoral Fellow, 1979-1980.

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X-ray Structural Analysis of $H_3[Rh_4(bridge)_8Cl][CoCl_4]_4 \cdot nH_2O$. The Photoactive Species in the Production of Hydrogen from Aqueous Solutions

Sir:

The photochemical production of hydrogen gas from aqueous solutions has recently been an extremely active research area. Several hydrogen producing systems have been designed and investigated by different workers.[1] The central point in these investigations has been the determination of the mechanism for hydrogen formation from photogenerated precursors. As an aid to illucidating the mechanism of photochemical hydrogen production in the $Rh_2(bridge)_4^{2+}$ (bridge

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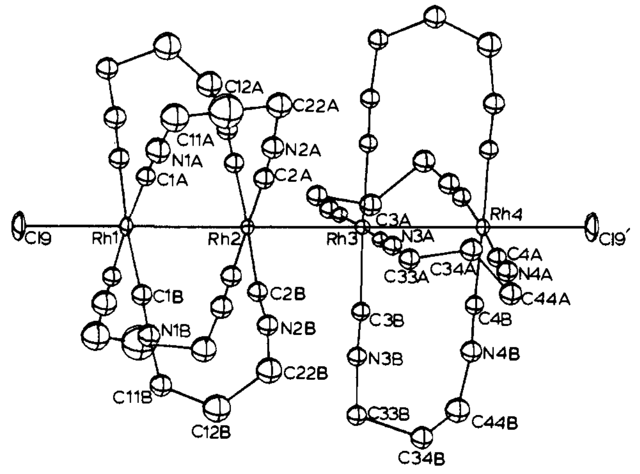

Figure 1. View of the structure of the $[Rh_4(bridge)_8Cl]^{5+}$ cation. Thermal ellipsoids are drawn at the 50% level. Cl(9) from the next unit cell is included.

= 1,3-diisocyanopropane) system,[2] we have previously determined the structures of the precursor $Rh_2(bridge)_4(BPh_4)_2{\cdot}CH_3CN$[3] and the photolysis product in HCl, $[Rh_2(bridge)_4Cl_2]Cl_2{\cdot}8H_2O$.[3] However, the structural characterization of the photoactive complex present in concentrated HX(aq) (X = Cl, Br, HSO_4) solutions has been somewhat indirect. Recently obtained chemical evidence[4] suggested that the formulation of the redox level of the Rh atoms was $+1\frac{1}{2}$, between the +1 determined for $Rh_2(bridge)_4)_2{\cdot}CH_3CN$[3] and +2 for $[Rh_2(bridge)_4Cl_2]Cl_2{\cdot}8H_2O$.[3] Flash photolysis studies[5] suggested that the photoactive complex was tetranuclear, consisting of two $Rh_2(bridge)_4{}^{3+}$ binuclear units. Infrared and elemental analyses are also consistent with this formulation.[6-8] Finally, evidence for halide binding[9] and the presence of a $\sigma \rightarrow \sigma^*$ transition[10] in the active complex led to its most recent formulation as $[Rh_2(bridge)_4]_2{}^{6+}$ in H_2SO_4 solutions and $[Rh_2(bridge)_4X]_2{}^{4+}$ in aqueous HX solutions,[5] the two binuclear units being held together by a Rh-Rh bond. We have now completed an X-ray crystallographic analysis of the salt obtained on addition of $CoCl_2{\cdot}6H_2O$ to the photoactive solution of $Rh_2(bridge)_4(BF_4)_2$ in 12 M HCl. We believe that the photoactive species in 12 M HCl differs from the cation present ($[Rh_4(bridge)_8Cl]^{5+}$) in this salt only by the binding of an additional Cl^- ion.

The dark green crystals obtained from these solutions[11] are monoclinic, space group $P2/n$ with $a = 16.005$ (4) Å, $b = 13.885$ (3) Å, $c = 19.432$ (9) Å, $\beta = 91.10$ (5)°, $Z = 2$, $\mu \approx 20.6$ cm^{-1}, $\rho_{calcd} = 1.626$ g cm^{-3} (for $H_3[Rh_4(bridge)_8Cl][CoCl_4]_4{\cdot}6H_2O$);[11] 4129 independent reflections were collected in the scan range $0° < 2\theta_{Mo\ K\bar{\alpha}} < 48.2°$ on an Enraf-Nonius CAD-4 automatic diffractometer using graphite monochromatized radiation employing the θ-2θ scanning technique. Calculations were performed on a PDP 11/45 computer using the Enraf-Nonius SDF program library. The structural parameters have been refined to convergence [$R = 0.076$ for 2372 independent reflections for which $F^2 > 2.0\sigma(F_o{}^2)$] in cycles of full-matrix least-squares refinement which employed anisotropic thermal parameters for the Rh, Co, and Cl atoms; C, N, and O atoms were given isotropic thermal parameters.

There are two symmetry-related tetranuclear complex ions of the form $[Rh_4(bridge)_8Cl]^{5+}$ per unit cell with the linear $[Rh_4Cl]$ units precisely aligned along the b crystallographic axis. The remaining contents of a unit cell consist of eight $CoCl_4{}^{2-}$ anions and several apparently disordered $[H^+{\cdot}nH_2O]$ cations (vide infra).

The tetranuclear rhodium complex (Figures 1 and 2) is made up of two binuclear $Rh_2(bridge)_4{}^{3+}$ units linked by a Rh-Rh bond. The Cl^- ion bridges the $Rh_4(bridge)_8{}^{6+}$ units to form a rigorously linear infinite chain of repeat unit (Rh_4Cl). The two binuclear $Rh_2(bridge)_4{}^{3+}$ units have approximately eclipsed ligand systems [the dihedral angles are 0 (1)° for the Rh(1)-Rh(2) binuclear unit and 12 (1)° for the Rh(3)-Rh(4) binuclear unit] similar to those previously found in $[Rh_2(bridge)_4Cl_2]Cl_2{\cdot}8H_2O$ and $Rh_2(bridge)_4(BPh_4)_2{\cdot}CH_3CN$,[3] but are nearly perfectly staggered with respect to each other [the dihedral angle is 46 (1)°]. The Rh-Rh bond distance between binuclear units [Rh(2)-Rh(3)] is 2.775 (4) Å, while the two Rh-Rh distances [Rh(1)-Rh(2) and Rh(3)-Rh(4)] within the binuclear units are 2.932 (4) and 2.923 (3) Å, respectively. The Rh-Rh bond distances within the binuclear units are intermediate to those found in the binuclear d^8d^8 compound $Rh_2(bridge)_4(BPh_4)_2{\cdot}CH_3CN$ [no formal Rh-Rh bond present, Rh(I)-Rh(I) distance of 3.263 (1) Å] and in the binculear d^7d^7 compound $[Rh_2(bridge)_4Cl_2]Cl_2{\cdot}8H_2O$ [a single Rh-Rh bond, Rh(II)-Rh(II) distance of 2.837 (1) Å]. This is consistent with a binuclear unit $Rh_2(bridge)_4{}^{3+}$ (d^8d^7) which contains (formally at least) a bond of order one half.[13] The Rh-Rh distance of 2.775 (4) Å between binuclear units is shorter than the Rh(II)-Rh(II) distance in the $Rh_2(bridge)_4Cl_2{}^{2+}$ ion which has the eclipsed configuration and is comparable with the Rh(II)-Rh(II) distance found in $[Rh_2(p\text{-}CNC_6H_4CH_3)_4I_2](PF_6)_2$ [Rh(II)-Rh(II) distance of 2.785 Å][12] which has a ligand conformation rotated 26° away from perfectly eclipsed. As previously discussed,[3] the staggered conformation should be the sterically preferred one, since it reduces the strong repulsive forces produced by the close contact of the π bond electron clouds of the CN groups.

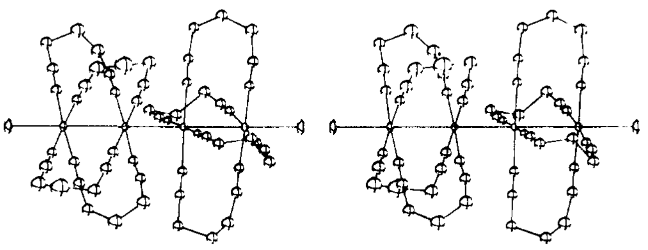

Figure 2. Stereoview of the structure of the $[Rh_4(bridge)_8Cl]^{5+}$ cation. Cl(9) from the next unit cell is included.

The Cl^- ion [Cl(9)] linearly bridges Rh(1) and Rh(4) of the next unit cell giving nearly identical distances of 2.613 (8) and 2.643 (9) Å, respectively. These Rh-Cl bonds are somewhat longer than those found in $Rh_2(bridge)_4Cl_2{}^{2+}$ [Rh-Cl distance of 2.447 (1) Å], consistent with the observation that Cl^- binding is stronger for $Rh_2(bridge)_4{}^{4+}$ than for $Rh_4(bridge)_8{}^{6+}$ in aqueous solution.[14]

The eight bridging isocyanide groups complete the coordination about the Rh atoms giving average Rh-C bond lengths of 1.96 (6) Å, C-N bond lengths of 1.14 (2) Å, and Rh-CN bond angles of 175 (4)°. These values are similar to ones determined for other bridged binuclear rhodium diisocyanide complexes.[3]

The $CoCl_4{}^{2-}$ anions appear to be completely unexceptional, the average Co-Cl bond lengths of 2.26 (1) Å and Cl-Co-Cl bond angles of 109 (4)°, close to those found in Cs_3CoCl_5[15] of 2.252 (12) Å and 108.6°.

Deserving of comment is the unfortunate presence of apparent disorder in the $[H^+{\cdot}nH_2O]$ ions which carry the remaining positive charges in the unit cell. It was initially hoped that the charge balance in the unit cell could be used to unambiguously confirm the chemical assignment of oxidation level in the tetranuclear $Rh_4(bridge)_8{}^{6+}$ ion. This confirmation of oxidation level cannot at this time be made from the crystallographic data alone, owing to insufficient and/or poor quality of the data needed to define a suitable model to treat the small peaks of electron density (≤ 1 e/Å^3) which apparently are due to the oxygen atoms of disordered $[H^+ \cdot nH_2O]$ ions. At least one of these ions (an $H_5O_2^+$ ion) is *not* disordered yielding reasonable thermal parameters and an O(1)–O(1) hydrogen bonded distance of 2.45 (5) Å, similar to those found in other structures containing this ion.[16] Hydrogen bonds are formed between this ion and Cl(1D) [3.20 (2) Å] and Cl(2A) [2.99 (2) Å]. Partially occupied oxygen atoms [O(2) and O(3)] were also placed from difference Fourier maps, their positional and thermal parameters refined with their occupancy factors fixed at 0.5. Reasonable temperature factors were obtained in this way, but full confidence cannot be placed on the values for the parameters of these atoms. In spite of the difficulties arising from the disordering problem of the $[H^+ \cdot nH_2O]$ ions, the reasonable values obtained for the Rh–Rh bond distances and the overwhelming chemical evidence[4,8] give us confidence that the formal oxidation level is indeed 1½ for each of the four Rh atoms in the tetranuclear unit, giving an overall charge of +5 to the $Rh_4(bridge)_8Cl^{5+}$ unit. This requires the formula to be $H_3[Rh_4(bridge)_8Cl](CoCl_4)_4 \cdot nH_2O$, where n is at least 3 and more likely 6.

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Supplementary Material Available: Final atomic coordinates and thermal parameters (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) For example: (a) DeLaive, P. J.; Sullivan, B. P.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1979,** *101*, 4007–4008. (b) Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *Ibid.* **1979,** *101*, 1298–1300. (c) Lehn, J.-M.; Sauvage, J.-P. *Nouv. J. Chim.* **1977,** *1*, 449–451.

(2) (a) Mann, K. R.; Lewis, N. S.; Miskowski, V. M.; Erwin, D. K.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1977,** *99*, 5525–5526. (b) Gray, H. B.; Mann, K. R.; Lewis, N. S.; Thich, J. A.; Richman, R. M. *Adv. Chem. Ser.* **1978,** No. 168, 44–56. (c) Mann, K. R.; Gray, H. B. *Ibid.* **1979,** No. 173, 225–235.

(3) The crystal structures of these complexes have been determined. $Rh_2(bridge)_4(BPh_4)_2 \cdot CH_3CN$: Reference 1b. Mann, K. R.; Thich, J. A.; Bell, R. A.; Coyle, C. L.; Gray, H. B., to be submitted for publication. $[Rh_2(bridge)_4Cl_2]Cl_2 \cdot 8H_2O$: Reference 1c. Mann, K. R.; Bell, R. A.; Gray, H. B. *Inorg. Chem.* **1979,** *18*, 2671–2673.

(4) In a typical experiment 0.012 mmol of $Rh_2(bridge)_4{}^{2+}$ produced 0.005 mmol of H_2 upon reaction with 12 M HCl (5 mL) in the dark. Irradiation ($\lambda > 520$ nm) of the resulting blue solution yielded an additional 0.006 mmol of H_2. In 6 M HCl, 1 equiv of Cr^{2+} reduces $Rh_2(bridge)_2Cl_2{}^{2+}$ to the blue species $[Rh_4(bridge)_8Cl]^{5+} + Cl^-$, and 2 equiv of Ce^{4+} ($+Cl^-$) oxidizes $[Rh_4(bridge)_8Cl]^{5+}$ back to $2Rh_2(bridge)_4Cl_2{}^{2+}$: Mann, K. R.; Sigal, I. S.; Gray, H. B., submitted for publication.

(5) Miskowski, V. M.; Sigal, I. S.; Mann, K. R.; Gray, H. B.; Milder, S. J.; Hammond, G. S.; Ryason, P. R. *J. Am. Chem. Soc.* **1979,** *101*, 4383–4385.

(6) Dart, J. W.; Lloyd, M. K.; Mason, R.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1973,** 2039–2045.

(7) Lewis, N. S.; Mann, K. R.; Gordon, J. G., II: Gray, H. B. *J. Am. Chem. Soc.* **1976,** *98*, 7461–7463.

(8) The infrared spectra of model rhodium isocyanide complexes in the $\bar{\nu}$(CN) region are as follows: Rh(I) complexes, $[Rh(CN\text{-}t\text{-}Bu)_4]Cl$, 2164 cm^{-1} (KBr pellet)[6] and $Rh_2(bridge)_4(BPh_4)_2 \cdot CH_3CN$, 2172 cm^{-1} (KBr pellet);[7] binuclear Rh(II) complexes, $[Rh_2(bridge)_4Cl_2]Cl_2$, 2246 cm^{-1} (Nujol mull), and $[Rh_2(bridge)_4I_2](I_3)_2$, 2227 cm^{-1} (KBr pellet);[7] Rh(III) complexes, $[Rh(CN\text{-}i\text{-}Pr)_4Cl_2](PF_6)$, 2250 cm^{-1} (KBr pellet),[6] and $[Rh(CNCH_3)_4Cl_2](PF_6)$, 2280 cm^{-1} (KBr pellet).[6] These data suggest a rough correlation of the formal oxidation state of the Rh atoms with the position of $\bar{\nu}$(CN). Consistent with this correlation, $H_3[Rh_4(bridge)_8Cl][CoCl_4]_4 \cdot nH_2O$, which formally contains Rh(I½), shows a $\bar{\nu}$(CN) at 2221 cm^{-1} (Nujol mull) and a weak shoulder to the higher energy side of the band, placing it between the Rh(I) and Rh(II) model complexes. A dark blue ClO_4^- salt obtained by addition of $NaClO_4$ to blue aqueous HBr solutions of $Rh_2(bridge)_4(BF_4)_2$ analyzes for $Rh_2(bridge)_4(ClO_4)_3$. Calcd: C, 20.34; H, 2.22; N, 9.49; Cl, 18.01. Found: C, 20.41; H, 2.57; N, 9.47; Cl, 17.97. This salt also shows a $\bar{\nu}$(CN) region (2228 cm^{-1}, weak shoulder to higher energy, Nujol mull) virtually identical with that found for $H_3[Rh_4(bridge)_8Cl][CoCl_4]_4 \cdot nH_2O$.

(9) The Cl^- binding constant determined in aqueous 0.1 M HSO_3CH_3 by making plots of the equation $\log \{[Rh_4(bridge)_8Cl_n]^{(6-n)+}/[Rh_4\,(bridge)_8{}^{6+}]\} = \log K + n \log [Cl^-]$ gives $n = 1.0 \pm 0.1$, and $\log K = 2.8 \pm 0.2$ at 25 ± 1 °C, maximum $[Cl^-] = 0.01$ M. Binding of an additional Cl^- at the high $[Cl^-]$ present in 12 M HCl solutions is also likely to occur.

(10) The strong visible absorption band ($\lambda_{max} \approx 558$ nm) exhibited by $Rh_4(bridge)_8Cl^{5+}$ in 12 M HCl solution, upon cooling, shows the characteristic hypsochromic shift and increase in ϵ_{max} associated with the $\sigma \rightarrow \sigma^*$ transitions found in compounds which contain single metal–metal bonds. See Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975,** *97*, 6042–6047. The extremely low position energetically for this transition must at least in part be due to delocalization of the transition over all four Rh atoms.

(11) Crystals of this complex were obtained with extreme difficulty. Evaporation of the 12 M HCl solution was carried out in a desiccator in which were placed a beaker of P_2O_5 (to remove H_2O) and a beaker of NaOH pellets (to remove HCl). The solutions are slowly air and light sensitive. The green crystals obtained become opaque *seconds* after removal from the mother liquor. Most of the crystals in a batch grow as flat crosses. The crystal used in this study was mounted in a capillary in a minimally lighted room by transferring a crystal in constant contact with the mother liquor to the wide end of the capillary which was also opened at the opposite end. The crystal was then forced into the capillary until it wedged by causing mother liquid to flow through the capillary. Both ends of the capillary were then sealed with epoxy. Once mounted in this way, the crystal was stable, mechanically and chemically, as evidenced by the lack of observable movement or decomposition during the data collection. Density measurements (flotation in CCl_4–1,1,2,2-tetrabromoethane) depend on how long the crystals have been removed from the mother liquor. For crystals removed for longer than 1 week $\rho_{obsd} = 1.79$ (1) g cm^{-3}; for crystals taken directly from the mother liquor, $\rho_{obsd} = 1.7$ (1) g cm^{-3}; during this measurement (~10 min) the crystals had also become opaque, probably with solvent loss. ρ_{calcd} for $Z = 2$, $H_3[Rh_4(bridge)_8Cl](CoCl_4)_4 \cdot 6H_2O$, = 1.626 g cm^{-3}.

(12) Olmstead, M. M.; Balch A. L. *J. Organomet. Chem.* **1978,** *148*, No. 178, C15–C18.

(13) Although this analysis suggests that the oxidation states of the Rh atoms can best be represented by Rh(I)Rh(II)Rh(II)Rh(I), it is recognized that a molecular orbital description of the bonding along the RhRh axis would be more appropriate, the resonance structure suggested here being the dominant one.

(14) Mann, K. R., unpublished result.

(15) Figgis, B. N.; Gerloch, M.; Mason, R. *Acta Crystallogr.* **1964,** *17*, 506–508.

(16) Schuster, P.; Zundel, G.; Sandorfy, C. "The Hydrogen Bond"; North-Holland Publishing Co.: Amsterdam, 1972; Vol. II, Chapter 10, pp 473–526.

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Selective Enhancement of Bimolecular Reaction Rates by Over Three Orders of Magnitude Using Low Intensity CW Infrared Laser Radiation

Sir:

Chemists are understandably intrigued by the possibility of selective *unimolecular* dissociation processes using pulsed high power infrared lasers.[1] The fervor in this field somewhat overshadows the equally interesting possibility of utilizing infrared lasers to selectively modify *bimolecular* reaction rates.[2] We report here the use of a relatively low power (34 W/cm²) CW infrared laser to increase selectively the rate constant of a single bimolecular reaction by three orders of magnitude in a complex system, thus achieving a situation which is distinctly nonthermal. The reacting species are gas-phase ions which are generated, stored for periods up to 1 s, and detected using the techniques of ion cyclotron resonance (ICR) spectroscopy. Full details of ICR spectroscopy,[3,4] including modifications for infrared photochemistry,[5] are published elsewhere.

The equilibrium

$$(CH_3OH)H^+(OH_2) + CH_3OH \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (CH_3OH)_2H^+ + H_2O \quad (1)$$

is characterized by forward rate constant $k_f = 5.0 \times 10^{-10}$ cm³ mol⁻¹ s⁻¹ and reverse rate constant $k_r = 8.2 \times 10^{-15}$ $cm^3\ mol^{-1}\ s^{-1}$. k_f is measured using ICR techniques, whereas k_r is calculated from k_f and the equilibrium constant K. The value $\Delta G = -6.5 \pm 1.0$ kcal/mol[6,7] for reaction 1 gives $K = 6.1 \times 10^4$ in favor of proton-bound methanol dimer, $(CH_3OH)_2H^+$, at room temperature.

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