mechanism presumably involves the addition of a proton to the central bond followed by the cyclobutyl–cyclopropylcarbinyl rearrangement of the resulting 2,6-methano-2-norbornyl cation to the 2,6-dehydro-1-norbornylcarbinyl cation, which reacts with a chloride ion to give **5**.

Contrary to the normal carbon–carbon single bond, the central bond in propellane **2** appears to be highly sensitive to both free radicals and acids. The high reactivity of the central bond has been observed also for other [3.1.1]propellanes,[9,10] as well as for [4.1.1]-,[6] [3.2.1]-,[7] and [2.2.2]propellanes.[8a] This is in good agreement with the high electron density at the back side of the inverted carbon predicted theoretically[4,5] for small-ring propellanes. However, further studies are necessary for better understanding the nature of bonding between inverted carbon atoms. We suggested recently[24] that such bonding in smallest ring propellanes was actually a limiting form of the carbon–carbon single bond, while the other limiting form was the bond between two sp^3-hybridized carbon atoms. All other carbon–carbon single bonds should necessarily lie between these two extremes.

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Registry No. 1a, 50682-95-6; **1b**, 81830-74-2; **2**, 81830-75-3; **2a**-*8,8-d₂*, 81830-81-1; **3**, 81830-76-4; **4a**, 81830-78-6; **4b**, 81830-79-7; **5**, 81830-80-0; 6-norbornanone-2-*endo*-carboxylic acid, 42392-37-0; 6-norbornanone-2-*endo*-carboxylic acid dimethylamide, 81830-72-0; 6-(dimethylamino)methyl-2-norbornanol, 81830-73-1; 6-(dimethylamino)-methyl-2-norbornanol amine oxide, 81846-83-5; 6-methylene-d_2-2-norbornanone tosylhydrazone sodium salt, 81830-77-5; oxygen, 7782-44-7; carbon tetrachloride, 56-23-5; tosyl chloride, 98-59-9; hydrogen chloride, 7647-01-0.

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(23) **5**: ^{13}C NMR ($CDCl_3$) δ 48.8 (t, 1 C), 35.3 (t, 1 C), 34.1 (t, 2 C), 31.6 (d, 1 C), 25.9 (s, 1 C), 18.9 (d, 2 C); ^1H NMR ($CDCl_3$) δ 3.83 (s, 2 H), 2.1–1.1 (m, 9 H); IR (film) 3050, 2960, 2860, 1440, 790 cm^{-1}; MS *m/e* 145(3), 144 (M^+, 4), 143 (6), 142 (M^+, 10), 107 (30), 91 (31), 80 (39), 79 (100).

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Catalytic Oxidation of Water by an Oxo-Bridged Ruthenium Dimer

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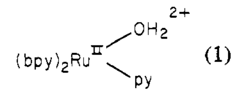
In recent work the properties of an oxo/aquo system of ruthenium were reported (eq 1; the reduction potentials refer to pH



(1)

7 vs. the saturated sodium chloride calomel electrode (SSCE) at 25 °C; py = pyridine; bpy = bipyridine).[1] The initial impetus for the work was to develop possible catalytic systems for the oxidation of water, in part because of an interest in photochemical methods for catalytically splitting H_2O into H_2 and O_2.[2] On the basis of single sites, the oxo–ruthenium complexes have not led to the catalytic oxidation of water but have been of interest for their ability to act as catalysts for the oxidation of organic substrates[3] and for the mechanistic details of their reactions.[4] In one case, that involving the Ru(VI) complex $(bpy)_2RuO_2^{2+}$, a *stoichiometric* oxidation of H_2O has been observed that appears to occur via H_2O_2 as an intermediate.[5] We report here on an oxo-bridged dimeric system of ruthenium(III), $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$, which upon oxidation by 4 equiv, leads to the rapid oxidation of water and provides a basis for the catalytic oxidation of water.

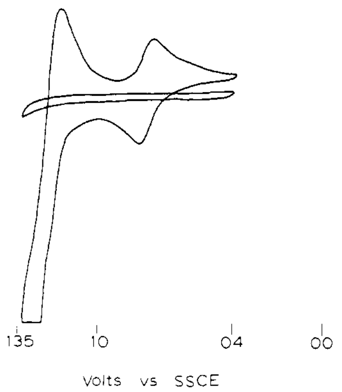


Figure 1. Cyclic voltammogram of $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$ in 0.1 M H_2SO_4 taken by using a glassy carbon working electrode and SSCE reference electrode. The scan rate was 100 mV/s.

When $(bpy)_2Ru(H_2O)Cl^+$, formed by the hydrolysis of $(bpy)_2RuCl_2$, is heated at reflux in H_2O for 1 h in the presence of 2.5 equiv of $AgNO_3$, the solution turns deep blue. A blue solid can be isolated from the solution as either the ClO_4^- or the PF_6^- salt, which as the ClO_4^- salt, analyzes well for $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2](ClO_4)_4{\cdot}4H_2O$.[6] The oxo-bridged formulation seems reasonable given similarities in the optical spectrum of the product when compared to the spectra of the related dimers $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ and $[(bpy)_2(NO_2)RuORu(NO_2)(bpy)_2]^{2+}$.[9] The structure of the latter complex is known,[10] and the aquo dimer is readily converted into the nitro dimer in aqueous solution at room temperature by the addition of NO_2^- (eq 2). The Ru(III), Ru(III) aquo dimer can be oxidized quantitatively by one electron (electrochemically or via Ce(IV) oxidation) to give a stable Ru(III), Ru(IV) dimer (λ_{max} 494 nm at pH 1.1; ϵ 17 200).

In Figure 1 is depicted a cyclic voltammogram of the Ru(III), Ru(III) aquo dimer in 0.1 M H_2SO_4. The (Ru(III), Ru(IV))/

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(6) The product reported here is *not* the green solid isolated first by Dwyer[7] and later by Weaver.[8] When dissolved, the green solid is *not* a catalyst for the oxidation of water. Anal. Calcd for $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]{\cdot}(ClO_4)_4{\cdot}4H_2O$: C, 35.61; H, 3.81; N, 8.31. Found: C, 35.68; H, 3.69; N, 8.09.

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(9) Data (wavelengths in nm) for the Cl and NO_2 dimers are taken from Weaver.[8] (1) $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$ in CH_3CN: λ_{max} 672, ϵ 17 900; λ_{max} 289, ϵ 39 000; λ_{max} 244, ϵ 65 900. (2) $[(bpy)_2(NO_2)RuORu(NO_2)(bpy)_2]^{2+}$ in CH_3CN: λ_{max} 632, ϵ 25 700; λ_{max} 284, ϵ 48,900; λ_{max} 244, ϵ 38 400. (3) $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$ in H_2O: λ_{max} 640, ϵ 16 200; λ_{max} 284, ϵ 59 000; λ_{max} 245, ϵ 41 300.

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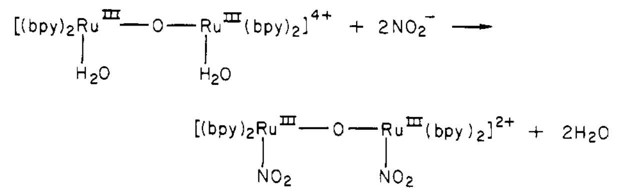


$$[(bpy)_2\underset{H_2O}{\underset{|}{Ru^{III}}}-O-\underset{H_2O}{\underset{|}{Ru^{III}}}(bpy)_2]^{4+} + 2NO_2^- \longrightarrow [(bpy)_2\underset{NO_2}{\underset{|}{Ru^{III}}}-O-\underset{NO_2}{\underset{|}{Ru^{III}}}(bpy)_2]^{2+} + 2H_2O \quad (2)$$

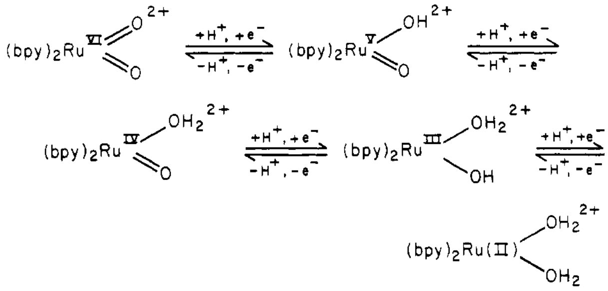
(Ru(III), Ru(III)) couple appears at 0.77 V (vs. SSCE). A second wave appears at 1.20 V, the oxidative component of which appears as a shoulder on a larger catalytic wave involving oxidation of the solvent. Note the solvent background in the absence of dimer and the fact that electrolysis in the presence of dimer leads to visible evolution of O_2 at the electrode.

We have observed that the Ru(III), Ru(III) dimer can also act as a catalyst in the chemical oxidation of H_2O. Upon addition of 50-fold and 100-fold excesses of Ce(IV) to solutions containing 4.1×10^{-5} M dimer in 0.1 M $HClO_4$, O_2 appears rapidly and in the amounts expected based on reaction 3 as monitored by gas

$$4Ce(IV) + 2H_2O \xrightarrow[\text{catalyst}]{\text{Ru}} 4Ce(III) + O_2 + 4H^+ \quad (3)$$

chromatography. At the end of the catalytic experiments the dimer was present in its Ru(III), Ru(IV) form as shown spectrophotometrically (λ_{max} 494 nm; ϵ 17 200). With even greater excesses of added Ce(IV), the catalytic ability of the system is eventually lost, apparently due to a breakdown in the dimeric structure. Simple mixing experiments show that addition of 4 equiv of Ce(IV) results in a rapid loss of color followed by a reappearance of color (as the Ru(III), Ru(IV) dimer) both on a time scale of seconds or less. The appearance of O_2 seems to be concomitant with the reappearance of color. The reaction is currently under investigation with use of stopped-flow spectrometry.

There are several available facts that when combined provide a basis for a reasonable understanding of the ability of the dimeric system to oxidize H_2O: (1) The crystal structure of the analogous nitro dimer shows that groups like NO_2 or H_2O are held in close proximity and can approach van der Waals contact distances by allowed molecular motions.[10] It has been concluded that strong electronic coupling across the oxo group exists between ruthenium ions in related oxo-bridged dimers.[8] (2) It is known that higher oxidation states of ruthenium are accessible by a series of sequential electron–proton losses, as observed most dramatically in the $(bpy)_2Ru(H_2O)_2^{2+}$ system[5] (eq 4). Studies of the pH dependences of $E_{1/2}$ values for the dimer over the pH range 0.0–4.6 reveal that the (Ru(III), Ru(IV))/(Ru(III), Ru(III)) and (Ru(IV), Ru(IV))/(Ru(III), Ru(IV)) couples shift reductively by approximately 59 mV/pH decade, suggesting a similar sequence of electron–proton losses for the dimer (eq 5 and 6). It should be stressed, however, that the precise locations of the protons in the dimer are not known at this point, and only the proton content is. (3) Rapid evolution of oxygen occurs only upon addition of 4 or more equiv of Ce(IV), suggesting that the active entity is a four-electron oxidizied intermediate and that there may be two additional one-electron couples following eq 5 and 6.

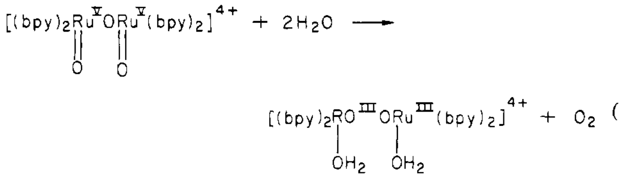


(4)

$$[(bpy)_2(OH)Ru^{IV}ORu^{III}(H_2O)(bpy)_2]^{4+} + H^+ + e^- \rightarrow [(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+} \quad (5)$$

$$[(bpy)_2(OH)Ru^{IV}ORu^{IV}(OH)(bpy)_2]^{4+} + H^+ + e^- \rightarrow [(bpy)_2(OH)Ru^{IV}ORu^{III}(H_2O)(bpy)_2]^{4+} \quad (6)$$

Given the structural, redox, and reactivity properties of related Ru=O "ruthenyl" systems, we suggest that the reaction may involve an initial four-electron oxidation to give a Ru(V), Ru(V) dimer, which in turn gives O_2 in a concerted four-electron step (eq 7). The mechanism of the reaction is currently under investigation.



$$[(bpy)_2\underset{O}{\underset{\|}{Ru^{V}}}O\underset{O}{\underset{\|}{Ru^{V}}}(bpy)_2]^{4+} + 2H_2O \longrightarrow [(bpy)_2\underset{OH_2}{\underset{|}{RO^{III}}}O\underset{OH_2}{\underset{|}{Ru^{III}}}(bpy)_2]^{4+} + O_2 \quad (7)$$

The reaction is not confined to the bpy dimer; the analogous 1,10-phenanthroline (phen) dimer, $[(phen)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(phen)_2]^{4+}$, also acts as a catalyst toward the oxidation of water. It is clear that we will be able to vary the redox potentials of the catalyst by varying substituents on the ligands.

The results reported here are notable in that the dimeric Ru complexes may provide models both for the oxygen-evolving site in photosynthesis, which is thought to involve a Mn dimer,[11] and for surface reactions of RuO_2,[12] where the oxidation of water to oxygen is facile and the oxidation of chloride to chlorine is of commercial importance. It is of interest to note that, when oxidized, the oxo-bridged ruthenium dimers also carry out the oxidation of chloride to chlorine in acidic solution, and clearly they will prove to have an extensive chemistry as oxidants.

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Registry No. $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2](ClO_4)_4$, 56110-88-4; H_2O, 7732-18-5; Ce, 7440-45-1.

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Alicyclic Claisen Rearrangement. A General Carbocycle Synthesis Based on Four-Atom-Ring Contractions of Lactones

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The Claisen rearrangement has enjoyed extensive application in organic synthesis, primarily in the stereocontrolled synthesis of cyclic natural products or acyclic substructural units.[1] In contrast to these examples, the reaction has seen limited application in the construction of the *carbocyclic* ring systems of natural products.[2] However, the exceptional syntheses of aphidicolin and

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