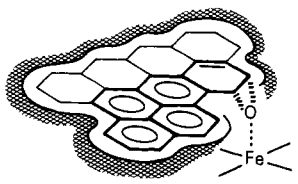

Figure 1. Estimated shape of the hydrophobic depression that constitutes the catalytic binding site of cytochrome P-450c. Only one of the heterotopic faces of benzo[*a*]pyrene can face the heme and fit into the site if the 9,10-bond of the hydrocarbon is epoxidized.

more polar (*S,S*)-diastereomers always show these hydrogens as a pair of AB quartets with $J_{gem} \sim 16$ Hz for each ester. In **1B** the hydrogens within each CH_2 group are nonequivalent and each CH_2 appears at a pair of AB quartets (centered at δ 3.72 and 3.93 and at δ 3.86 and 4.04 with $J_{gem} \sim 16$ Hz) suggestive of an *S,S* configuration. For **1A** these hydrogens appear as a sharp singlet (δ 3.98) and a weakly split AB quartet (major lines at δ 3.83 and 3.86) suggestive of an *R,R* configuration. After hydrolysis (50% 1 N NaOH in THF/MeOH (1:1), 18 °C, 2 h) of **1A**, the resultant free tetrahydrodiol (+)-**2** [mp 165 °C, $[\alpha]_D$ +55° (7 mg/mL, THF)] was benzoylated quantitatively (benzoyl chloride in pyridine, 10 °C, 18 h) to afford (−)-**3** [mp 145–146 °C, $[\alpha]_D$ −50° (30 mg/mL, $CHCl_3$)]. Bromination at C-7 with *N*-bromosuccinimide (in CCl_4) followed by dehydrohalogenation and hydrolysis with NaOMe [in THF/MeOH (1:1), 18 °C, 3 h] afforded (−)-**4** [mp 210 °C, $[\alpha]_D$ −294° (5 mg/mL, THF), HPLC on a Du Pont Zorbax ODS column (21.2 × 250 mm) eluted with 75% MeOH in water, $k' = 4.2$] in 77% overall yield for the above three steps (Scheme I). The circular dichroism spectrum of the (−)-9,10-dihydrodiol ((−)-**4**) was identical with that of 9,10-dihydrodiol formed metabolically from benzo[*a*]pyrene.[9]

Unequivocal assignment of the 9*R*,10*R* configuration to compounds **1A** and (−)-**4** (Scheme I) was achieved by (i) epoxidation of the dihydrodiol (−)-**4** to form a pair of diastereometrically related 9,10-diol 7,8-epoxides in which the benzylic 10-hydroxyl group is either cis or trans to the epoxide oxygen and (ii) acid-catalyzed hydrolysis of the trans isomer at C-7 to form a tetraol of known absolute configuration (Scheme II). Epoxidation of (−)-**4** with *m*-chloroperoxybenzoic acid as described for the racemic material[10] afforded a 2:3 mixture of the cis and trans diastereomers from which the trans isomer (*trans*-**5**) could be isolated in pure form by crystallization from tetrahydrofuran. The other diastereomer (*cis*-**5**) required HPLC for final purification.[11] Acid-catalyzed hydrolysis of *trans*-**5** (20% THF in 0.1 M $NaClO_4$ adjusted to pH 2.5 with $HClO_4$, 1 h, 18 °C) proceeded mainly by trans addition of water at C-7 to afford the *trans,cis,trans*-tetraol (+)-**6**, which was isolated in pure form by HPLC on a Du Pont Zorbax ODS column (21.2 × 250 mm^2) eluted with 60% methanol in water [$k' = 3.2$, $[\alpha]_D$ +51° (3 mg/mL in THF)]. The opposite enantiomer of the *trans,cis,trans*-tetrol [(−)-**6**: $[\alpha]_D$ −49° (3 mg/mL in THF), circular dichroism band $\Delta\epsilon_{340} = -1.32$ (methanol)] was obtained as the major product upon similar acidic hydrolysis but at C-10 of the known[5a] trans-diastereomer (+)-benzo[*a*]pyrene-(7*R*,8*S*)-diol (9*S*,10*R*)-epoxide. Acidic hydrolysis of *cis*-**5** by trans addition of water at the 7-position provided the *trans,trans,trans*-tetraols [(+)-**7**: $[\alpha]_D$ +110° (5mg/mL in THF), $k' = 3.9$]. Definitive structural assignments of the enanthiomeric tetraols rests on comparison of their HPLC retention time, UV spectra, mass spectra, and NMR spectra of their tetraacetates with the corresponding data for the racemic tetraol.[12]

The above correlations establish *trans*-**5** as the (9*S*,10*R*)-diol (7*R*,8*S*)-epoxide and *cis*-**5** as the (9*S*,10*R*)-diol (7*S*,8*R*)-epoxide. Furthermore, (−)-**4**, which is metabolically formed from benzo[*a*]pyrene,[9,13] must be the (−)-(9*R*,10*R*)-dihydrodiol. Since labeling studies have shown that the C-9 hydroxyl group derives from water and the C-10 hydroxyl group derives from air in the 9,10-dihydrodiol,[13,14] cytochrome P-450c must form predominantly the (9*S*,10*R*)-arene oxide which epoxide hydrolase[15,16] converts to the (−)-(9*R*,10*R*)-dihydrodiol.

On the basis of the known absolute configurations of several benzo[*a*]pyrene metabolites[5,9,17,18] and the assumption that a superimposition of all of these must fit into the active site of cytochrome P-450c in such a way that the double bond that is epoxidized lies directly over the heme iron, we have proposed[4] that the shape of the catalytic binding site for this enzyme is approximated by the hypothetical hydrocarbon shown in Figure 1. The model predicts that the (9*S*,10*R*)-arene oxide should be formed (dark outline in the hypothetical hydrocarbon skelton, Figure 1) and subsequently converted to the (9*R*,10*R*)-dihydrodiol by epoxide hydrolase, as confirmed by the present study. We felt that assignment of abolute configuration to the metabolically formed 9,10-dihydrodiol would provide a good test of this model since previous workers had erroneously predicted[13] that this dihydrodiol would have a 9*S*,10*S* absolute configuration.

Registry No. 1A, 81987-41-9; **1B**, 82041-88-1; (+)-**2**, 82041-89-2; (+)-**3**, 82041-90-5; (−)-**4**, 62600-11-7; *cis*-**5**, 64937-37-7; *trans*-**5**, 64937-38-8; (+)-**6**, 82041-91-6; (−)-**6**, 75110-13-3; (+)-**7**, 75110-16-6.

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(11) The THF mother liquor of crystallization from which the pure (9*S*,10*R*)-diol (7*R*,8*S*)-epoxide (*trans*-**5**) was removed was subjected to further purification by HPLC [Du Pont Zorbax SIL column (6.2 × 250 mm^2) eluted with 40% THF in hexane, recycled five times] to provide the pure (9*S*,10*R*)-diol (7*R*,8*R*)-epoxide (*cis*-**5**); NMR (100 MHz, acetone-*d*) δ 4.48 (H_7), 4.10 (H_8), 4.76 (H_9), 5.60 (H_{10}), with $J_{7,8} = 4.2$, $J_{8,9} = J_{9,10} = 2.5$, and $J_{9,10} = 2.5$ H_2. The NMR spectrum of *trans*-**5** was a previously reported.[10]

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2,6-Methano-2,6-dehydronorbornane: An Exceptionally Strained [3.1.1]Propellane[1]

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We report the first synthesis, characterization, and chemical behavior of a new [3.1.1]propellane, 2,6-methano-2,6-dehydronorbornane[2] (**2**). This is the most strained carbocyclic propellane that has been prepared.

Small-ring propellanes are tricyclic systems with three rings fused to a common, central bond containing two inverted carbon atoms.[3] Both the molecular orbital[4] and maximum overlap[5]

(1) Presented in part at the 10th Northeast Regional Meeting of the American Chemical Society, July 1980, Potsdam, NY, and at the 7th Meeting of Chemists of Croatia, February 1981, Zagreb, Yugoslavia.

(2) Tetracyclo[3.2.1.0.^{1,3}O^{3,7}]octane.

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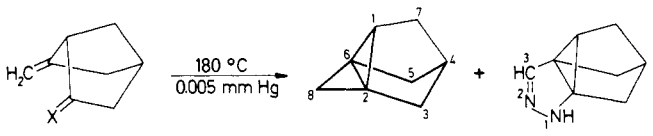
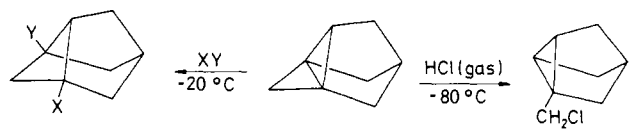
Scheme I



Scheme II



calculations indicate a high electron density at the back side of the inverted carbon atoms and a decrease in electron density in the region of the central bond. This unusual shift of electron density should be particularly large for smallest ring propellanes. Propellane systems containing six bridge carbons ([4.1.1],[6] [3.2.1],[7] and [2.2.2][8]) have been prepared in the last decade and were found to be very reactive. Recently we prepared the first carbocyclic [3.1.1]propellane, highly reactive 2,4-methano-2,4-dehydroadamantane,[9] and soon afterwards Gassman and Proehl[10] reported a synthesis of the parent [3.1.1]propellane.[11] Neither of these two [3.1.1]propellanes possesses any significant additional strain relative to that in the [3.1.1]propellane unit itself.

2,6-Methano-2,6-dehydronorbornane (**2**) is considerably more strained than the parent [3.1.1]propellane owing to the additional methano bridge, which stretches both the bicyclobutane and cyclopentane ring. The strain energy difference is estimated to be 15–20 kcal/mol.[13]

Propellane **2** was prepared by the intramolecular cycloaddition of 6-methylene-2-norbornylidene to the olefinic bond. This methology has been used by us[9] and recently by Hamon and Trenerry[6b] for the preparation of other [*n*.1.1]propellanes. The synthesis of **2** originated with 6-norbornanone-2-*endo*-carboxylic acid.[15] The acid was readily converted into the dimethylamide, which was reduced by $LiAlH_4$ to 6-*endo*-(dimethylamino)-methyl-2-norbornanol. Hydrogen peroxide oxidation of the amine to the amine oxide followed by pyrolysis of the latter and PCC oxidation afforded 6-methylene-2-norbornanone (**1a**)[16] in 20% overall yield (based on the acid). Pyrolysis of the dry tosylhydrazone sodium salt **1b** derived from ketone **1a** at 180 °C in vacuo (Scheme I) produced 50% of a 2:1 mixture of 2,6-methano-2,6-dehydronorbornane (**2**) and the dihydro-1*H*-pyrazole derivative **3**. The latter is, in fact, a diaza[3.3.1]propellene.[17] The products sublimed into a trap cooled by liquid nitrogen and were analyzed by ^{13}C NMR spectroscopy. The possible elimination product, 6-methylene-2-norbornene, was not detected. Propellane **2** (90% pure by ^{13}C NMR) was isolated by resublimation from approximately −30 °C to a liquid-nitrogen-cooled trap at 0.02 mmHg. Product **3** (80–90% pure by ^{13}C NMR) remained as the residue.

The proofs for the structure of **2** are based on the mass, ^1H NMR, and ^{13}C NMR spectra [six signals: dd, d, d, t, t (2 C), s (2 C)].[18] The C–H coupling constants of the ^{13}C NMR dd signal at δ 65.5 (149 and 171 Hz) are typical of the methylene carbon in the bicyclobutane system.[19b] This signal is absent in the ^{13}C NMR spectrum of 2,6-methano-2,6-dehydronorbornane-*8,8-d*$_2$ (**2a**),[21] which provides additional evidence for the structure of **2**.

2,6-Methano-2,6-dehydronorbornane (**2**) is thermally less stable than 2,4-methano-2,4-dehydroadamantane. The former decomposed completely within 30 min at room temperature in C_6D_6 solution, while the latter decomposed by less than 10% in 3 h under the same conditions. Propellane **2** reacted at −20 °C readily with oxygen and instantaneously with neat carbon tetrachloride and tosyl chloride in chloroform, yielding the corresponding 2,6-disubstituted 2,6-methanonorbornanes (**4a**, **4b**; Scheme II).[22] No other definable products were detected in appreciable amounts. These reactions are probably free-radical ones, and the products arise from additions to the central bond. With gaseous hydrogen chloride neat **2** reacted readily at −80 °C, yielding a single product, 1-(chloromethyl)-2,6-dehydronorbornane (**5**, Scheme II).[23] The

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(10) Gassman, P. G.; Proehl, G. S. *J. Am. Chem. Soc.* **1980**, *102*, 6862.

(11) An oxa[3.1.1]propellane derivative was prepared previously by Szeimies et al.[12a] Very recently the same group reported syntheses of an aza[3.1.1]propellane derivative[12b] and a highly substituted carbocyclic [3.1.1]propellane.[12c]

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(13) The strain energy of **2** was calculated to be 88.6 kcal/mol by using the MM2 force field,[14a] while that of the parent [3.1.1]propellane was estimated[14b] to be 70 kcal/mol.

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(15) Beckmann, S.; Geiger, H. *Chem. Ber.* **1961**, *94*, 48.

(16) (a) **1a**: ^{13}C NMR ($CDCl_3$) δ 211.9 (s), 143.4 (s), 109.5 (t), 60.4 (d), 43.4 (t), 38.3 (t), 36.1 (t), 34.6 (d); MS *m/e* 122 (M^+, 28%), 79 (100), 78 (52), 77 (30). (b) Ketone **1a** was prepared recently in a low yield by pyrolysis of 6-(acetoxymethyl)norbornan-2-one ethylene ketal at 500 °C followed by hydrolysis (Werstiuk, N. H.; Taillefer, R. *Can. J. Chem.* **1978**, *56*, 1134).

(17) Heterocyclic propellene **3** was identified by the ^{13}C NMR spectrum [(C_6D_6) δ 142.2 (d), 55.1 (s), 43.9 (d, very small *J*), 37.2 (d), 36.0 (t), 33.94 (t), 33.92 (t), 12.5 (d)], the ^1H NMR spectrum [(C_6D_6) δ 6.8 (s, 1 H), 5.6 (very br s, 1 H), 1.8 (br s, 1 H), 1.5–1.0 (m, 6 H), 0.4 (br s, 1 H)], the IR spectrum [(CCl_4) 3380, 3050, 2945, 2865, 1445, 1260, 1085 cm^{-1}], and the MS spectrum [*m/e* 134 (M^+, 35%), 133 (30), 119 (68), 106 (28), 105 (28), 92 (41), 91 (100)]. It is probably formed by tautomerization of the initially produced dihydro-3*H*-pyrazole derivative, the intramolecular cycloadduct of the intermediary 6-methylene-2-diazonorbornane.

(18) MS *m/e* 106 (M^+, 1.7%), 105 (1.5), 92 (78), 91 (100), 67 (59); ^1H NMR (C_6D_6/furan 1:1, −30 °C) δ 3.08 (d, *J* = 3.9 Hz, 1 H, HC-8), 2.74 (dd, *J* = *J'* = 3.5 Hz, 1 H, HC-8), 2.51 (s, 1 H, HC-1), 2.22 (br s, 1 H, HC-4), 1.45 (d, *J* = 11.8 Hz, 2 H, HC-3,5), 1.3 (s, 2 H, HC-7), 0.68 (d, *J* = 11.8 Hz, 2 H, HC-3,5); the chemical shifts are assigned by the coupling constants and homo and selective decoupling. ^{13}C NMR (C_6D_6/furan 1:1, −30 °C) δ 65.5 (dd, *J* = 149, 171 Hz, 1 C, C-8), 56.2 (d, *J* = 189 Hz, 1 C, C-1), 44.8 (d, 1 C, C-4), 37.01 (t, 1 C, C-7), 36.96 (t, 2 C, C-3, C-5), 21.5 (s, 2 C, C-2, C-6). The bicyclobutane carbon atoms are strongly deshielded relative to the corresponding atoms in nortricyclane.[19a] This may be explained by the balance[20a] of the inverted carbon hybridization deshielding,[20b] the bicyclobutane shielding of the central carbons and deshielding of the outer atoms,[20c] as well as by the change in the mutual influence of the neighboring carbons.

(19) (a) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 63. (b) p 335.

(20) (a) Majerski, Z.; Mlinarič-Majerski, K.; Meić, Z. *Tetrahedron Lett.* **1980**, 4117. (b) Duddeck, H.; Klein, H. *Ibid.* **1976**, 1917. Pincock, R. E.; Fung, F.-N. *Ibid.* **1980**, 19. (c) Christl, M. *Chem. Ber.* **1975**, *108*, 2781.

(21) Compound **2a** was prepared by pyrolysis of the tosylhydrazone sodium salt of 6-methylene-d_2-2-norbornanone.

(22) **4a**: ^{13}C NMR ($CDCl_3$) δ 104.0 (s), 60.4 (s), 57.6 (s), 55.5 (d), 49.9 (dd), 48.0 (t), 39.15 (t), 39.06 (d), 38.1 (t); ^1H NMR ($CDCl_3$) δ 3.3–3.1 (m, 2 H), 2.65 (br s, 1 H), 2.35–1.5 (m, 7 H); IR (film) 2970, 2950, 2870, 1450, 1140, 787, 772, 753 cm^{-1}; MS *m/e* 262 (M^+, 0.5), 260 (M^+, 0.8), 258 (M^+, 0.7), 224 (15), 222 (15), 149 (65), 147 (100). **4b**: ^{13}C NMR ($CDCl_3$) δ 144.8 (s), 133.8 (s), 129.8 (d), 128.7 (d), 61.2 (s), 61.1 (s), 54.9 (d), 47.74 (t), 47.71 (t), 39.2 (d), 37.7 (t), 36.6 (t), 21.6 (q); ^1H NMR ($CDCl_3$) δ 7.68 (d, 2 H), 7.33 (d, 2 H), 3.5–1.1 (m, 13 H); IR (KBr) 3065, 2965, 2870, 1450, 1312, 1302, 1287, 1148, 678 cm^{-1}; MS *m/e* 296 (M^+, 10%), 141 (80), 105 (100), 91 (62), 79 (72).

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.

Acknowledgment. This work was supported by a grant from the Research Council of the Republic of Croatia (SIZ II). We thank Drs. Z. Meić and N. Blaževič for recording the ^{13}C NMR and mass spectra, respectively.

Registry No. 1a, 50682-95-6; **1b**, 81830-74-2; **2**, 81830-75-3; **2a**-*8,8-d*$_2$, 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.

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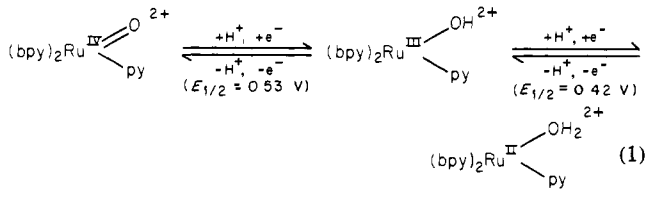
In recent work the properties of an oxo/aquo system of ruthenium were reported (eq 1; the reduction potentials refer to pH



(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.

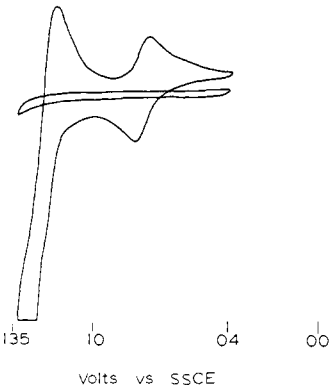


Figure 1. Cyclic voltammogram of $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$ in 0.1 M H_2SO_4 taken by using a glassy carbon working electrode and SSCE reference electrode. The scan rate was 100 mV/s.

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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