signals range from 0.1–0.3 and increase as the temperature lowers. Finally, an empirical model based on PM3 conformational analysis permits a tentative assignment of configurations at the carbon atom α to the metal, relative ligand on the basis of both anisotropic effects and free energy criteria. Structural studies aimed at finding definitive proof for the assignment of the absolute configuration as well as studies of other organometallic species are underway.

Experimental Section

Organozinc bromides were obtained by reaction of active zinc with the corresponding bromides, previously distilled over P_2O_5, in dry THF at RT in an Ar atmosphere.[21]. (*R*)-**1** and (*S*)-**1** were purified by precipitation with $ZnCl_2$ (THF), extraction (0.2 M aqueous NaCN in $CHCl_3$), and vacuum distillation. (*RS*)-**1** ($[\alpha]^{25}_{D} = 0.0$) was prepared by mixing equal amounts of the former reagents. The concentration in all the NMR experiments was 0.5 M in THF/C_6D_6 (1/1), except for those performed at 150 °C in which it was 1.5 M in THF/[D_8]THF (4/1). TMS was added as an internal standard.

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[15] Deconvolution and analytical integration of signals was performed throughout, both for superposed and nonsuperposed peaks. The ratios were compared for two sets of signals belonging to the same molecule (for example, Me and α-H), the deviation being <2 % in all cases.

[16] In conditions of intermediate exchange (for example, Figure 2 d) the spectra obtained at ≤10 °C showed broad signals for both diastereomers in a ratio only slightly smaller than that observed at −30 °C.

[17] The analyses were performed using HyperChem 5.1 pro from Hypercube Inc., 1998 and compared with the results obtained with CS MOPAC pro from Cambridge Soft Corporation, 1998. Essentially identical differences in conformational energies were found in all cases.

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[19] $\Delta S^0 = \Delta S^0_{\text{rot.}} + \Delta S^0_{\text{vibr.}} + \Delta S^0_{\text{sym.}} + \Delta S^0_{\text{mix.}}$. From these, the rotational and vibrational contributions can usually be neglected to a first approximation and the entropy of symmetry is equal to 0.

[20] For example, the 2-octylzinc bromide prepared from (*R*)-2-bromooctane in ref. [2b] has now been unambiguosly identified as racemic by using this method.

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Electrochemical Oxidation of Water to Dioxygen Catalyzed by the Oxidized Form of the Bis(ruthenium–hydroxo) Complex in H_2O**

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Much attention has been paid to the oxidation of water to dioxygen by homogeneous catalysts. Of particular interest are di- and tetranuclear transition metal complexes, since extended X-ray absorption fine structure studies have indicated that the O_2-evolving center (OEC) in photosystem II is composed of a tetranuclear Mn cluster with dimeric di-μ-oxo Mn units.[1] A variety of di- and tetranuclear metal complexes have been prepared as structural models of the OEC, and four-electron oxidation of water has been attained with only a few dinuclear metal (Mn, Ru) complexes.[2–4] The key intermediates for O_2 evolution in the OEC is thought to be high-valent metal–oxo complexes derived from aqua

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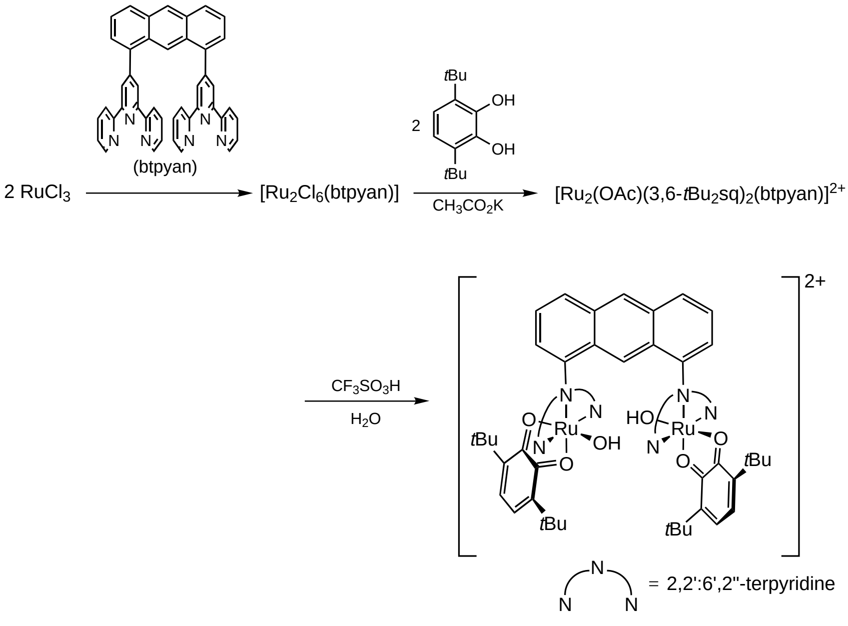
complexes.[5] We have reported that, depending on the pH of the media, the aqua ligand of $[\mathrm{Ru(OH_2)(quinone)(terpy)}]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) leads to dissociation of protons without formation of a μ-oxo dimer.[6] The dinuclear complex $[\mathrm{Ru^{II}_2(OH)_2(3,6\text{-}}t\mathrm{Bu_2qui)_2(btpyan)](SbF_6)_2}$ (3,6-tBu$_2$qui = 3,6-di(*tert*-butyl)-1,2-benzoquinone, btpyan = 1,8-bis{(2,2′:6′,2″)-terpyridyl}anthracene) was thus prepared, with the aim of converting two H_2O molecules into oxo ligands at a vicinal position in the complex to form the O–O bond. Herein we report an effective oxidation of water that is catalyzed by the indium-tin-oxide (ITO) electrode modified with the bis(ruthenium–hydroxo) complex in water.



Scheme 1. Synthesis of the bis(ruthenium–hydroxo) complex.

The bis(ruthenium–hydroxo) complex was prepared by three reactions as shown in Scheme 1. $[\mathrm{Ru_2Cl_6(btpyan)}]$, prepared by the reaction of $\mathrm{RuCl_3}$ with 1,8-bis(terpyridyl)anthracene (btpyan) in MeOH, was treated with 3,6-di(*tert*-butyl)-1,2-benzocathechole in the presence of potassium acetate in MeOH. The resulting μ-acetato complex $[\mathrm{Ru^{II}_2(OAc)(3,6\text{-}}t\mathrm{Bu_2sq)_2(btpyan)}]^{+}$ (3,6-tBu$_2$sq = 3,6-di(*tert*-butyl)-1,2-semiquinone)[7] was treated with triflic acid in MeOH containing water, and then sodium hexafluoroantimonate was added to the reaction mixture to give the bis(ruthenium–hydroxo) complex.[8] The total yield over three steps was 29 % based on the amount of $\mathrm{RuCl_3}$ used.

The electronic absorption spectra of the bis(ruthenium–hydroxo) complex in MeOH showed a strong band at 576 nm. The addition of two equivalents of tBuOK to the solution resulted in the loss of the band at 576 nm and the appearance of a new band at 850 nm in the spectrum. Moreover, acidification of the solution by the addition of two equivalents of $\mathrm{HClO_4}$ completely restored the band at 576 nm and the 850 nm band disappeared. On the basis of the electronic absorption spectra of the mononuclear ruthenium(II)–quinone complex[6, 9] the bands at 576 nm and 850 nm are reasonably assigned to the metal-to-ligand charge-transfer (MLCT) bands of ruthenium(II)–quinone and ruthenium(II)–semiquinone complexes, respectively. The acid–base equilibrium of the $\mathrm{OH_2}$ group of $[\mathrm{Ru(OH_2)(Q)(terpy)}]^{2+}$ has been shown to be coupled with the reduction of the quinone (Q) to the semiquinone (SQ).[6] The change in the electronic absorption spectra in the present study is therefore ascribed to the acid–base equilibrium between $[\mathrm{Ru(OH)(3,6\text{-}}t\mathrm{Bu_2qui)Ru(OH)(3,6\text{-}}t\mathrm{Bu_2qui)}]^{2+}$ and $[\mathrm{Ru(O)(3,6\text{-}}t\mathrm{Bu_2sq)Ru(O)(3,6\text{-}}t\mathrm{Bu_2sq)}]^{0}$ coupled with the ligand-localized redox reaction [Eq. (1)]. The rest potential of the solution of

$$[\mathrm{Ru(OH)(3,6\text{-}}t\mathrm{Bu_2qui)Ru(OH)(3,6\text{-}}t\mathrm{Bu_2qui)}]^{2+} \xrightleftharpoons[+2\mathrm{H}^+]{-2\mathrm{H}^+} [\mathrm{Ru(O)(3,6\text{-}}t\mathrm{Bu_2sq)Ru(O)(3,6\text{-}}t\mathrm{Bu_2sq)}]^{0} \quad (1)$$

$[\mathrm{Ru(OH)(3,6\text{-}}t\mathrm{Bu_2qui)Ru(OH)(3,6\text{-}}t\mathrm{Bu_2qui)}]^{2+}$ in MeOH was +0.49 V (versus Ag/AgCl).[10] The cyclic voltammogram of the complex showed two redox couples at $E_{1/2} = +0.43$ and +0.35 V in MeOH [Eq. (2)]. The conversion of $[\mathrm{Ru(OH)(3,6\text{-}}t\mathrm{Bu_2qui)Ru(OH)(3,6\text{-}}t\mathrm{Bu_2qui)}]^{2+}$ into $[\mathrm{Ru(O)(3,6\text{-}}t\mathrm{Bu_2sq)Ru(O)(3,6\text{-}}t\mathrm{Bu_2sq)}]^{0}$ by the addition of two equivalents of tBuOK to the MeOH solution [Eq. (1)] shifted the rest potential of the solution to −0.12 V. The redox process of the resultant oxo complex also displayed two nearly reversible redox couples at $E_{1/2} = +0.40$ and +0.30 V [Eq. (3)].

$$\begin{gathered}[\mathrm{Ru(OH)(3,6\text{-}}t\mathrm{Bu_2qui)Ru(OH)(3,6\text{-}}t\mathrm{Bu_2qui)}]^{2+} \xrightleftharpoons[+0.43\,\mathrm{V}]{e^-} \\ [\mathrm{Ru(OH)(3,6\text{-}}t\mathrm{Bu_2qui)Ru(OH)(3,6\text{-}}t\mathrm{Bu_2sq)}]^{+} \xrightleftharpoons[+0.35\,\mathrm{V}]{e^-} \\ [\mathrm{Ru(OH)(3,6\text{-}}t\mathrm{Bu_2sq)Ru(OH)(3,6\text{-}}t\mathrm{Bu_2sq)}]^{0}\end{gathered} \quad (2)$$

$$\begin{gathered}[\mathrm{Ru(O)(3,6\text{-}}t\mathrm{Bu_2qui)Ru(O)(3,6\text{-}}t\mathrm{Bu_2qui)}]^{2+} \xrightleftharpoons[+0.40\,\mathrm{V}]{e^-} \\ [\mathrm{Ru(O)(3,6\text{-}}t\mathrm{Bu_2qui)Ru(O)(3,6\text{-}}t\mathrm{Bu_2sq)}]^{+} \xrightleftharpoons[+0.30\,\mathrm{V}]{e^-} \\ [\mathrm{Ru(O)(3,6\text{-}}t\mathrm{Bu_2sq)Ru(O)(3,6\text{-}}t\mathrm{Bu_2sq)}]^{0}\end{gathered} \quad (3)$$

However, further oxidation of $[\mathrm{Ru(OH)(3,6\text{-}}t\mathrm{Bu_2qui)Ru(OH)(3,6\text{-}}t\mathrm{Bu_2qui)}]^{2+}$ and $[\mathrm{Ru(O)(3,6\text{-}}t\mathrm{Bu_2qui)Ru(O)(3,6\text{-}}t\mathrm{Bu_2qui)}]^{2+}$ was not detected in MeOH and acetone as a result of decomposition of the solvent. The present bis(ruthenium–hydroxo) complex was not soluble in water. We used an ITO electrode modified with the complex to study the redox behavior of the complex in water.[11] The electronic absorption spectra of the complex on a glass plate in water at pH 2.0 also showed the strong MLCT band at 578 nm. The intensity of the 578 nm band decreased and the band at 850 nm emerged with increasing pH. The ratio of the absorbances at 578/850 nm reached about 3/2 at pH 3.0, and became constant at higher pH values. This observation is explained by the reasoning that only the complex located in the vicinity of the surface of the modified electrode reversibly releases a proton from the aqua ligand, and is dependent on the pH value of the aqueous phase [Eq. (1)].

Figure 1 shows the cyclic voltammogram of the bis(ruthenium–hydroxo) complex modified on an ITO electrode (1.2×10^{-8} mol per 2.0 cm^2) in water (pH 4.0). The complex on the ITO electrode exhibited a broad redox couple centered at +0.40 V (versus Ag/AgCl), an irreversible anodic wave at +1.20 V, and a strong anodic current at potentials more positive than +1.5 V.[12] On the basis of the redox behavior of the complex in MeOH and the electronic absorption spectra of the complex on a glass plate, the broad anodic and cathodic waves centered at +0.40 V is reasonably assigned to the [Ru(OH)(3,6-*t*Bu$_2$qui)Ru(OH)(3,6-*t*Bu$_2$qui)]$^{2+}$/[Ru(OH)(3,6-*t*Bu$_2$sq)Ru(OH)(3,6-*t*Bu$_2$sq)]^0 and [Ru(O)(3,6-*t*Bu$_2$qui)Ru(O)(3,6-*t*Bu$_2$qui)]$^{2+}$/[Ru(O)(3,6-*t*Bu$_2$sq)Ru(O)(3,6-*t*Bu$_2$sq)]^0 redox reactions [Eqs. (2), (3)]. The irreversible anodic wave at +1.20 V is associated with two-electron oxidations of [Ru(OH)(3,6-*t*Bu$_2$qui)Ru(OH)(3,6-*t*Bu$_2$qui)]$^{2+}$ and [Ru(O)(3,6-*t*Bu$_2$qui)Ru(O)(3,6-*t*Bu$_2$qui)]$^{2+}$ that afford [Ru(OH)(3,6-*t*Bu$_2$qui)Ru(OH)(3,6-*t*Bu$_2$qui)]$^{4+}$ and [Ru(O)(3,6-*t*Bu$_2$qui)Ru(O)(3,6-*t*Bu$_2$qui)]$^{4+}$, respectively. The strong anodic current at potentials more positive than +1.5 V is apparently caused by the oxidation of water to dioxygen.

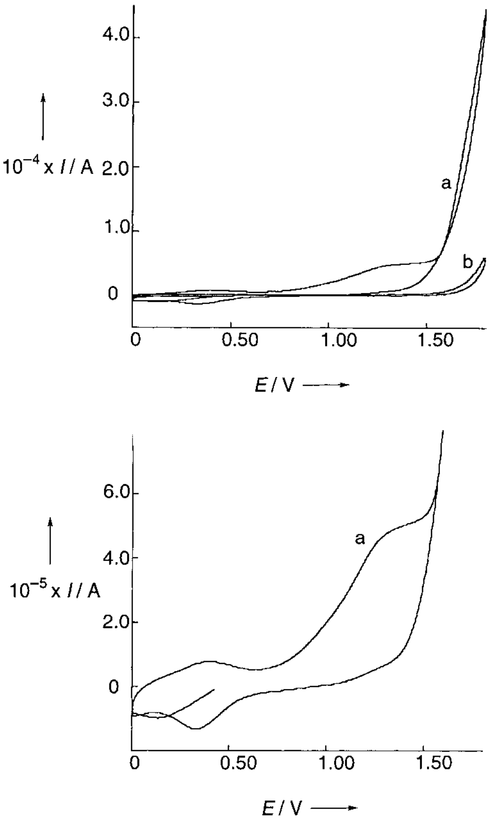


Figure 1. Cyclic voltammograms (versus Ag/AgCl) of the ITO electrode modified with the bis(ruthenium–hydroxo) complex (1.2×10^{-8} mol per 2.0 cm^2) (a) and an ITO electrode (b) in aqueous H_3PO_4/KOH solution (0.5 M) at pH 4.0.

Indeed, when a controlled-potential electrolysis of the bis(ruthenium–hydroxo) complex on an ITO electrode was conducted at +1.70 V (versus Ag/AgCl) in water (pH 4.0) 1.1 mL of O_2 evolved after 20.2 coulombs had passed in the electrolysis.[13] The current efficiency for O_2 evolution was 95% and the turnover number was 500 based on the complex. The current density of the electrode was 0.12 mA cm^{-2} in the initial stage. The current gradually decreased with a decrease in the pH of the aqueous phase and almost stopped at pH 1.2. The current density of the electrode for the oxidation of water recovered when the pH of the water was readjusted to 4.0 by the addition of aqueous KOH to the aqueous phase. The oxidation of water by the ITO electrode modified with the bis(ruthenium–hydroxo) complex finally evolved 15.0 mL of O_2 (turnover 6730) before the evolution completely stopped after 40 h.[14]

In contrast to the catalytic activity of the dinuclear complex toward the oxidation of water, the cyclic voltammogram of the mononuclear complex [Ru(OH$_2$)(3,5-*t*Bu$_2$qui)(terpy)](ClO$_4$)$_2$ displayed no catalytic current of water oxidation in H_2O at pH 4.0. This result indicates that the two ruthenium–hydroxo units in the bis(ruthenium–hydroxo) complex play the key role in the oxidation of water. Two hydroxo groups in the present bis(ruthenium–hydroxo) complex must be placed adjacently inside the cavity formed by two terpyridyl and two bulky 3,6-di(*tert*-butyl)-1,2-benzoquinone ligands. The formation of the O–O bond in the catalytic evolution of O_2 probably results from the intramolecular coupling of the two oxo ligands of the dinuclear oxo complex derived from the bis(ruthenium–hydroxo) complex. The two-electron oxidation of [Ru$^{\mathrm{II}}$(O)(3,6-*t*Bu$_2$qui)Ru$^{\mathrm{II}}$(O)(3,6-*t*Bu$_2$qui)]$^{2+}$ produces [Ru$^{\mathrm{III}}$(O)(3,6-*t*Bu$_2$qui)Ru$^{\mathrm{III}}$(O)(3,6-*t*Bu$_2$qui)]$^{4+}$. The electronic structure of the latter species would be expressed as a resonance hybrid between [(3,6-*t*Bu$_2$qui)Ru$^{\mathrm{III}}$O-ORu$^{\mathrm{III}}$(3,6-*t*Bu$_2$qui)]$^{4+}$ and [(3,6-*t*Bu$_2$qui)Ru$^{\mathrm{II}}$O=ORu$^{\mathrm{II}}$(3,6-*t*Bu$_2$qui)]$^{4+}$. We, therefore, propose that O_2 evolution is caused by the replacement of the O_2 unit in [(3,6-*t*Bu$_2$qui)Ru$^{\mathrm{II}}$O=ORu$^{\mathrm{II}}$(3,6-*t*Bu$_2$qui)]$^{4+}$ with two molecules of H_2O. In this mechanism the two Ru$^{\mathrm{II/III}}$ and two quinone/semiquinone redox couples must also contribute to oxidize two water molecules with four electrons.

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[7] The acetato complex showed no signal in the usual paramagnetic region of the ^{1}H NMR spectra. The electronic spectra of the acetato complex in MeOH exhibited the strong band at 845 nm attributed to an MLCT band of the Ru$^{\mathrm{II}}$-semiquinone complex. The electronic

structure of the acetato complex is consistent with the formula $[Ru_2(OAc)(3,6\text{-}tBu_2sq)_2(btpyan)]^+$.

[8] The bis(ruthenium–hydroxo) complex was prepared as follows: triflic acid (100 µL) was added to a solution of $[Ru_2(OAc)(3,6\text{-}tBu_2sq)_2(btpyan)](OAc)$ (150 mg, 0.11 mmol) in MeOH (10 mL), and the solution was stirred for 4 d at room temperature. After the addition of $NaSbF_6$, the solution was concentrated to 5 mL to give $[Ru_2(OH)_2(3,6\text{-}tBu_2qui)_2(btpyan)](SbF_6)_2$ as a violet powder (57% yield). ESI-MS: m/z: 659(M^{2+}); elemental analysis calcd for $C_{72}H_{72}N_6O_6F_{12}Ru_2Sb_2$: C 48.34, H 3.94, N 4.70; found: C 48.39, H 3.85, N 4.64; UV/Vis-NIR (in MeOH): $\lambda_{max} = 576$ nm ($\varepsilon = 5700\,\text{M}^{-1}\text{cm}^{-1}$). The oxidation of the semiquinone ligand of $[Ru_2(OAc)(3,6\text{-}tBu_2sq)_2(btpyan)]^+$ to the quinone ligand of $[Ru_2(OH)_2(3,6\text{-}tBu_2qui)_2(btpyan)]^{2+}$ during the reaction may be caused by O_2.

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[10] The rest potential (V_{rest}) is defined as $V_{rest} = E_{1/2} + \mathrm{R}T/n\mathrm{F}\ln([\mathrm{Ox}]/[\mathrm{Red}])$ (R: gas constant, T: temperature, n: number of electrons in redox reaction, F: Faraday constant, Ox: oxidized species, Red: reduced species). Thereby, the distribution of the oxidized and reduced complexes in solutions can be evaluated from the difference between V_{rest} and $E_{1/2}$.

[11] A solution of the bis(ruthenium–hydoroxo) complex in acetone was dropped on an ITO electrode by microsyringe, and dried at room temperature.

[12] The cyclic voltammogram was measured at $10\,\text{mV}\,\text{s}^{-1}$ in an H_3PO_3/KOH buffer solution (0.5 M) using an ITO electrode modified with the bis(ruthenium–hydroxo) complex (1.2×10^{-8} mol per 2.0 cm^2) as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl reference electrode.

[13] Two compartment cells separated by a Nafion membrane were filled with an H_3PO_4/KOH buffer solution (1.0 M, 60 mL) and He gas was bubbled into the solution to remove O_2 from the aqueous phase. Controlled-potential electrolysis was performed with the ITO electrode modified with the bis(ruthenium–hydroxo) complex (1.0×10^{-7} mol per 10 cm^2) as the working electrode, a platinum plate (2.0 cm^2) as the counter electrode, and an Ag/AgCl reference electrode. Evolved dioxygen was determined by GC measurement.

[14] The complex was completely detached from the ITO electrode in 40 h under the controlled-potential electrolysis conditions at +1.7 V in H_2O.

Designing a Helical Polymer that Reverses its Handedness at a Selected, Continuously Variable, Temperature[**]

Kap Soo Cheon, Jonathan V. Selinger,[*] and
Mark M. Green[*]

A new kind of stereochemical experiment only accessible with cooperative helical arrays has been designed by enforcing a competition between two *structurally different* nonracemic chiral molecules to control the helical sense of a polymer. The experiment, which has been analyzed by a statistical physical theory, allows the optical activity of the polymer, as a function of the composition of the competing units, to be set to zero at any temperature and then increases in magnitude, in a positive or negative direction, as the temperature deviates from the chosen value.

Since the polyisocyanates[1] have served as models for other helical systems,[2] a conformational state of considerable interest,[3] we have applied this idea by synthesizing the polymer from structurally different chiral units, which compete with each other favoring the left- and right-handed helical senses. Since the strength of the chiral biases of the competing units for their favored helical sense are different, they compensate each other at some relative proportion away from 50/50. Moreover, since the competing chiral biases depend on temperature in different ways, this compensation point also depends on temperature. Hence, a polymer of fixed composition can pass through the compensation point as a function of temperature, with its dominant helical sense switching between left- and right-handed. This phenomenon can be described theoretically by a variation of the one-dimensional random-field Ising model.[4]

Three monomer units (**1**–**3**) were used in this study.[5] Homopolymers synthesized entirely from the *R* enantiomers of **1**, **2**, and **3** show identical circular dichroism spectra in sign and form, thereby demonstrating a preference for the same helical sense.[6] This corresponds to a negative rotation at the sodium D line.[1, 5, 6]

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