

Electrochemistry of Thin Films Containing Diruthenium Complexes on Electrodes

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The electrochemistry of diruthenium complexes is of importance in studies of dimetal complexes since multiple oxidation states of diruthenium complexes can lead to a variety of unique functions.¹ Therefore, the controlled production of diruthenium complexes in multiple oxidation states in a variety of environments is important. The formation of thin films of dimetal complexes is also of interest from a fundamental and a practical point of view because supramolecular arrays based on dimetal building units such as molecular organometal wires are known.² Our current interest is focused on the construction of molecular electrode devices using diruthenium complex film materials that are easily tunable. A gel-like membrane of a tetra-*n*-octylphosphonium bromide ($4C_8P^+Br^-$) lipid analogue is known to provide a suitable microenvironment for examining the electrochemistry of these redox active molecules.³ An artificial lipid, dihexadecyldimethylammonium poly(styrene sulfonate) ($2C_{16}N^+PSS^-$), which forms water-insoluble multilamellar bilayer films with fundamental lipid bilayer characteristics, has been used as the electrode modifier⁴ and the same methodology is used in the present paper for examining the film electrochemistry of the diruthenium complexes (**1** – **4**) incorporated into matrices (see Figure 1). We describe here the novel finding that the electrochemistry of the diruthenium complex (**4**) under a carbon monoxide atmosphere can be tuned by changing between crystalline and liquid crystalline phases of an artificial lipid film of $2C_{16}N^+PSS^-$.

Experimental Section. Typical procedures for preparation of the modified electrodes are as follows: A 30 microliter portion of the diruthenium complex/matrix such as $4C_8P^+Br^-$, $2C_{12}PO_4H$ or $2C_{16}N^+PSS^-$ in chloroform ([diruthenium complex] = 0.25 mM and [matrix] = 4.75 mM) was placed on a basal plane pyrolytic graphite (BPG) electrode surface (geometric area, 0.36 cm²) and then air-dried. The modified electrode was then immersed in a 0.5 M KCl aqueous solution, followed by cyclic voltammetry measurements under an N₂ or CO atmosphere. A temperature-controlled electrochemical cell was used.

Results and Discussion. The complexes **1** – **4** at the $4C_8P^+Br^-$ modified electrode undergo a single oxidation corresponding to Ru_2^{6+}/Ru_2^{5+} , a reversible reduction assigned as Ru_2^{5+}/Ru_2^{4+} and an irreversible reduction which involves the Ru_2^{4+}/Ru_2^{3+} couple. The complexes **2** – **4** modified with the anionic lipid $2C_{12}PO_4H$ undergo a single oxidation assigned as Ru_2^{6+}/Ru_2^{5+} and a broad reduction assigned as Ru_2^{5+}/Ru_2^{4+} , both of which have low current intensities; cast films of **2** – **4** undergo an

irreversible Ru_2^{6+}/Ru_2^{5+} process with small current intensities and also show a broad Ru_2^{5+}/Ru_2^{4+} reduction. Results from thin-layer film electrochemistry in aqueous media suggest that the $4C_8P^+Br^-$ cationic matrix provides a more suitable microenvironment for examining the electrochemistry of the diruthenium complex than the anionic lipid or solely cast films by themselves on the electrode.

Temperature dependence experiments were conducted for $4/2C_{16}N^+PSS^-$ modified electrodes under N₂ and CO. The electrochemistry showed a strong temperature dependence; at low temperature the electrode gave almost no electrochemical communication attributable to the diruthenium complex, but the peak currents increased with temperature and had an observed break near 25 °C, a value which is very close to the phase transition of the bilayer films of $2C_{16}N^+PSS^-$ (26 °C). Furthermore, the peak current changes are reversible between 10 °C (low intensities) and 35 °C (high intensities). These results suggest that a temperature-driven “on-off” switch for the electrochemistry of the diruthenium complex **4** upon CO binding is possible. In other words, at low temperature, the lipid bilayer films are electrochemically inactive and CO binding is insensitive due to the rigid bilayer structure while at high temperature the bilayer structure is more fluid, conditions under which the films are electrochemically active and CO binding sensitive.

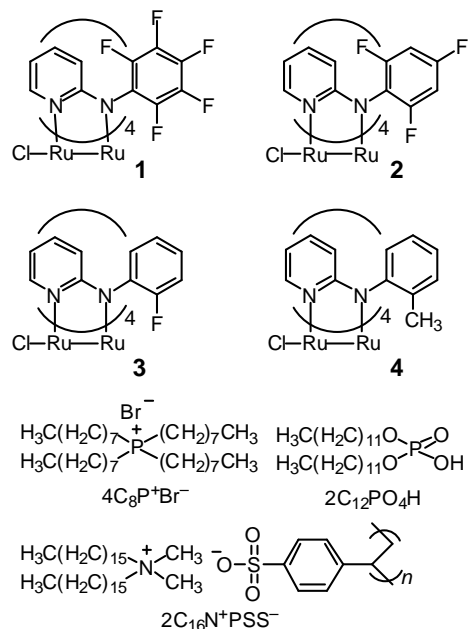


Figure 1. Chemical structures of diruthenium complexes (**1** – **4**) and matrices ($4C_8P^+Br^-$, $2C_{12}PO_4H$ and $2C_{16}N^+PSS^-$).

References:

- 1) Aquino M.S. *Coord. Chem. Rev.* **1998**, 170–141.
- 2) Wong, K.-T.; Lehn, J.-M.; Peng, S.-M.; Lee, G.-H. *Chem. Commun.* **2000**, 2259–2260.
- 3) Kadish, K. M.; Nakanishi, T.; Gürek, A.; Ahsen, V.; Yilmaz, I. *J. Phys. Chem. B* **2001**, 105, 9817–9821.
- 4) Nakashima, N.; Nonaka, Y.; Nakanishi, T.; Sagara, T.; Murakami, H. *J. Phys. Chem. B* **1998**, 102, 7328–7330.