Redox Behavior of *N,N'*-Ethylenebis(salicylideneaminato)-bis(triphenylphosphine)ruthenium(II)

Hideo Doine,* Francis F. Stephens, and Roderick D. Cannon†
College of Industrial Technology, Nihon University, 2-1 Izumicho, Narashino-shi, Chiba 275
†*School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England*

(Received October 1, 1984)

Synopsis. Visible spectra and electrochemical behavior of the title complex $[Ru\{C_2H_4(N{=}CHC_6H_4O\text{-}o)_2\}\{P(C_6H_5)_3\}_2]$ (**I**) are reported. The redox potentials of the ruthenium complex were determined at 25 °C to be $E^\circ = 0.27\pm0.01$ V (in CH_2Cl_2) and -0.161 ± 0.005 V (in CH_3OH), relative to $E^\circ(Fe(C_5H_5)_2)^{+/0}) = 0.400$ V.

In the previous electrochemical studies of binuclear complexes,[1] cyclic voltammetric data on ruthenium(II) Schiff-base complexes were reported. In this study, the redox potentials of the title compound **I** have been first measured and the compound was found to be a convenient reference material for testing the electrochemical cell system from the following fact: the title complex is soluble enough for the electrochemical measurement in both polar and nonpolar solvents, and the oxidation states of ruthenium ion in the complex **I** have no influence on the observed redox potentials. The complex was first synthesized by Thornback and Wilkinson[2] and found to be extremely air-sensitive. When the absorption spectra of the carefully prepared solutions of the complex **I** in deaerated solvents are compared with those previously reported,[3] it appears that the latter corresponds to an oxidized ruthenium(III) species. We have reinvestigated the preparation, handling and redox properties of the complex.

Preparation

The complex $RuCl_2(PPh_3)_3$[4] (0.20 g) was added under nitrogen to a solution of *N,N'*-ethylenebis (salicylideneamine) (H_2L)[5] (0.058 g) and Et_3N (1 ml) in THF in a flask having sintered glass filter-outlet already fitted. After refluxing 2 h some white solid was filtered off under nitrogen pressure. The solvent was removed, and the product was pumped dry, washed with petroleum (40—60°), and recrystallized under nitrogen by dissolving in a little THF and adding excess petroleum. The by-product Et_3NHCl was effectively removed in this way, mp 130—140°(dec). Found: C, 69.1; H, 5.07; N, 3.16%. Calcd for $C_{52}H_{44}N_2O_2P_2Ru$, C, 70.0; H, 4.94; N, 3.14%.

Results

Oxidation State. The complex **I** is readily oxidized by iodine and $FeCl_3$ in nonaqueous solvents but attempts to verify the stoichiometry by spectrophotometric and potentiometric titrations gave irreproducible results. This problem was overcome using a two-phase method as follows. An aliquot of **I** was weighed into a dry flask. The air was displaced with oxygen-free nitrogen, and a measured volume of a freshly prepared solution of resublimed iodine in methanol was added. After the reaction was complete (5 min were allowed) 5 ml of toluene was added, then an aliquot of aqueous sodium thiosulfate. After shaking, the aqueous layer was run off, and the organic phase was washed with water. The combined extracts were back-titrated with iodine in methanol using starch indicator. The iodine solution was standardized by direct titration with the $Na_2S_2O_3$, and the experiment was repeated with various amounts of **I** and iodine. Molar ratios [Ru complex (added)]/[I_2(consumed)] were found to be 1.94±0.09 from 10 titrations.

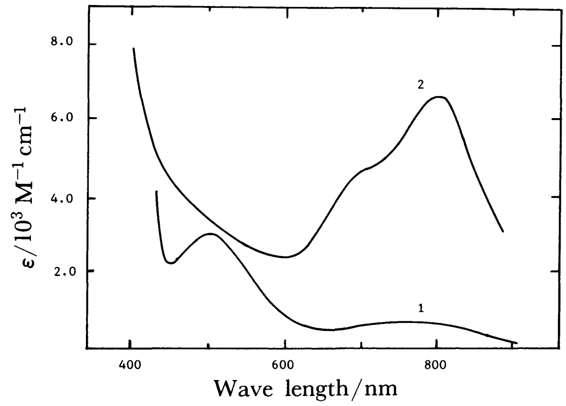

Fig. 1. Spectrum (1) of $RuL(PPh_3)_2$, and (2) of the product on air-oxidation, both in THF, where 1 M = 1 mol dm^{-3}.

Absorption Spectra and Electrochemical Properties. The purple-brown crystalline complex **I** is stable in air when dry, but for quantitative work it was stored under nitrogen. The solution in THF is pink-brown with $\lambda_{max}=770$ nm and 505 nm (Fig. 1). On admitting oxygen the THF solution changed rapidly to green with an increase in intensity, and the resulting absorption spectrum (2 in Fig. 1) was similar to that reported by West *et al.*[3] Similar color changes were noted in the solvents CH_2Cl_2 and MeOH, ease of oxidation increasing in the order THF<CH_2Cl_2<MeOH.

The spectra of oxidized and reduced forms have sharp isosbestic points (Fig. 2).

Cyclic voltammetry, in organic solvents under nitrogen, showed a single wave with equal anodic and cathodic peak heights, proportional to Ru concentration. The free ligand H_2L was inactive in the range studied (−0.8 to +0.9 V). The same signal was observed for both the solutions of **I** and air-oxidized form of **I**. On adding iodine, the anodic wave was supressed. In the presence of oxygen also, the anodic wave was supressed but on resuming the nitrogen flow the original peaks reappeared. The wave is assigned to the $Ru^{III/II}$ couple. In methanol, the couple is highly reversible, as judged by the peak-to-peak separations ΔE_{pp} and by the lack of dependence on scan rate. ($\Delta E_{pp}=60$ mV, scan rate 100 to 2000 mV s^{-1}, with 0.1

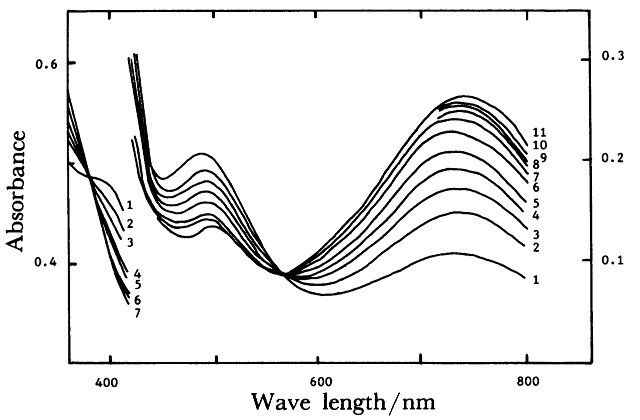

Fig. 2. Spectra (1) of RuL$(PPh_3)_2$, and (2—11) with successive addition of O_2. In methanol, $[Ru]_T$= 3.34×10^{-5} mol dm^{-3}, cell length of 1 cm.

mol dm^{-3} $NaClO_4$ supporting electrolyte. With 0.1 mol dm^{-3} [n-Bu_4N][BF_4], ΔE_{pp}=90 mV). In CH_2Cl_2, ΔE_{pp} increased from 120 mV at V=20 mV s^{-1} to 150 mV at 100 mV s^{-1}, and at 1000 mV s^{-1} another wave appeared at *ca.* −0.55 V. In THF the couple was found to be quasi-reversible, ΔE_{pp}=170 mV. Redox potentials were determined as $E_{1/2}$=0.27±0.01 V (in CH_2Cl_2); and $E_{1/2}$=−0.161±0.005 V (in MeOH, with 0.1 mol dm^{-3} n-$Bu_4N[ClO_4]$), based on E° $(Fe(C_5H_5)_2{}^{+/0})$=0.400 V.[6)]

This work was supported by the Royal Society and the Science and Engineering Research Council (UK). HD held a Monbusho Scholarship.

References

1) H. Doine, F. F. Stephens, and R. D. Cannon, *Inorg. Chim. Acta*, **75**, 135 (1983); **82**, 149 (1984).
2) J. R. Thornback and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, 110 (1978).
3) K. S. Murray, A. M. van den Bergen, and B. O. West, *Aust. J. Chem.*, **31**, 203 (1978).
4) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).
5) Gmelins Hanhbuch der anorganischen Chemie, 8th ed., "Kobalt," B, Supplement part 1 (1963), p. 206.
6) R. R. Gagné, C. A. Koval, and G. C. Lisensky, *Inorg. Chem.*, **19**, 2855 (1980).